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Review

Manipulating the self assembly of colloids in electric fields

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Abstract. During the last decade the focus in colloid science on self-assembly has moved from mostly spherical particles and interaction potentials to more and more complex particle shapes, interactions and conditions. In this minireview we focus on how external electric fields, which in almost all cases can be replaced by magnetic particles and fields for similar effects, are used to manipulate the self-assembly process of ever more complex colloids. We will illustrate typical results from literature next to examples of our own work on how electric fields are used to achieve a broad range of different effects guiding the self-assembly of colloidal dispersions. In addition, preliminary measurements and calculations on how electric fields can be used to induce lock-and-key interactions will be presented as well.

1 Introduction

Roughly coinciding with the start of this century there has been a strong increase in interest in studying the self-assembly (SA) [1] of colloids as is illustrated by references to papers reviewing this, almost exclusively from the last 5 year [2–28]. Also the number of review papers on the many aspects that deal with colloids in electric fields is impressive; for an incomplete list see Refs. [29–50]. This interest is still fueled both by significant increases in available synthesis routes to make monodisperse colloidal building blocks and the accompanying increases in possibilities these more complex colloids offer to tune the properties of materials based on their SA [2–54]. Necessarily and closely connected, although not always appreciated, is the need to better understand the fundamentals of the SA of more complex building blocks as well. As mentioned in the introduction of this collection of papers, an increased complexity is manifested both in more complex mixtures of particles, and also in more complex shapes and inter-particle interaction potentials of the systems in general. In addition, many groups designing colloidal particles are doing this with new functionality that can be realized with an ensuing self-assembly (SA) step and collective particle properties in mind. An example will perhaps make these points more concrete: The group of Nagao and Konno, partially together with our group, has for the last several years

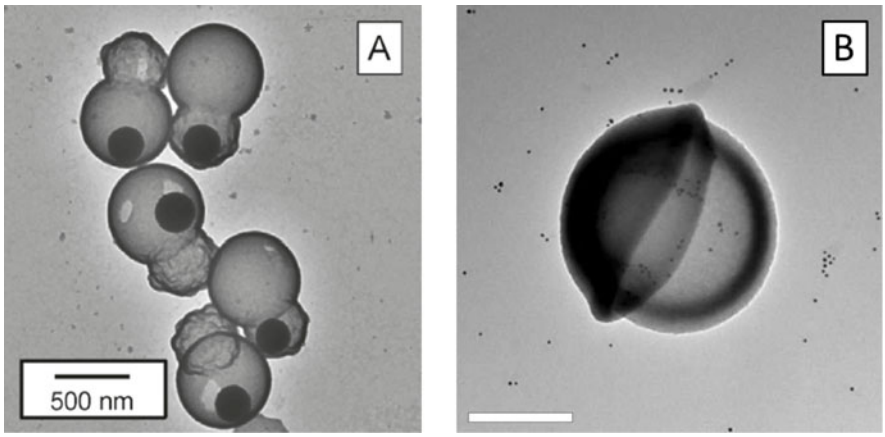

Fig. 1. Examples of particles designed with self-assembly in mind: (a) Silica shells with titania core particles movable in the shell [56] (b) Bowl-shaped particles made by buckling of spherical polydimethylsiloxane shells cross-linked using tetraethoxysilane that fit inside each other at high densities or induced attractions (see also Fig. 3c and 3d) [104]. Bars 500 nm.

been designing several core-shell-shell colloidal model systems with the intention to realize core-shell systems filled with liquid and freely movable cores inside an outer shell [55–59] see also Fig. 1a. Of course, colloidal particles with cores that can move by diffusion within a shell, which itself can also independently diffuse are interesting on their own right, but here these particles are specifically designed to be switchable after a further SA step: If such systems are made monodisperse enough they can be self-assembled to become part of a one-dimensional (1D), 2D or 3D lattice with a lattice constant similar to the wavelength of visible light. If, furthermore, the index of refraction of the outer shells of such photonic crystals would be matched to that of the solvent (inside and outside the particles), the resulting structures would have uniquely switchable optical properties: Without an external field the diffusion of the inner cores that scatter all the light would lead to significantly broadened Bragg peaks by what can be considered as a considerably broad Debye-Waller factor known for atomic and molecular crystals. However, an external electric field, in the case of dielectric spheres, or a magnetic field in the case of magnetic cores, could position the cores at well-defined positions within the shells and thus on the optical lattice and strongly sharpen the Bragg peaks. Both high index movable titania cores and magnetic cores were already realized not only in spherical shells [55] but also in more complex shaped particles such as asymmetric dumbbells [56–59].

The focus of this minireview is on the use of external electric fields to influence the SA of colloids. However, the example mentioned above on particles with movable cores makes it clear that in many cases what can be achieved with dielectric particles and electric fields can also be achieved with magnetic fields and magnetic particles [60]. Many groups have in the last decade come to the realization that with an increase in complexity of interaction potentials there is often an increase in necessity to tune or manipulate SA with external fields. A significant increase in the number of papers in which electric fields are used has ensued, which is illustrated by many review papers just in the last 5 years on the use of external fields in SA. We have therefore tried to cite most of these review papers instead of trying to cover all papers that appeared the last 5 years directly. In addition, we tried to illustrate the different uses of electric fields with typical examples from recent literature and our own work.

We also tried to categorize the papers and our typical examples along the lines of what the intended use of the external electric field was with respect to particle motion and/or interactions. For instance, homogeneous, direct current electric fields are known to directly couple to charged particles and the resulting motion is called electrophoresis, for which contributions to SA are given in the first section. Next, electric fields can also be used to polarize both charged and uncharged particles with the intention to couple these polarizations to the external field and/or to induce new interactions between the particles themselves, for instance to change their phase behavior. Induced dipoles in a homogeneous electric field can only orient an anisotropic particle; however, in a field gradient the resulting force and motion, called dielectrophoresis, can still be used to move colloids even if they are not charged. Thus electric field gradients are treated in the third subsection. Finally, a miscellaneous fourth section illustrates examples where electric fields are used in combination with other fields such as confinement or shear.

In cases where time varying electric fields are used we made a further subdivision based on a relaxation time of ions in a double layer. We distinguish frequencies chosen such that it is also the intention to induce polarization of the double layers of charged particles or of the double layers that build close to electrodes, and frequencies that are intended to be much higher than the relaxation rate of a double layer. Although light as an electromagnetic wave of high frequency falls clearly within the physics of the subject treated and has the strength of being able to manipulate individual colloids even in concentrated colloidal dispersions [52–54,61] it is not reviewed in the present paper for brevity and because it is dealt with in another minireview in this issue [62].

2 Moving charged particles in homogeneous electric fields

2.1 DC fields

As mentioned above, the motion of a charged particle caused by an electric field is termed electrophoresis. The reason electrophoresis was not chosen as the heading of this subsection is that it is strongly associated with the characterization of particle charge and not with SA. This is not to say that there is no significant progress in the field of electrophoresis for the characterization of particles. For instance, methods and theory have started focusing on electrophoresis of nanoparticles (see e.g. the recent reviews Refs. [40,41]). Also, the relatively old method of performing electrophoresis using a microscope, micro-electrophoresis, has recently been given a new twist by combining it with confocal microscopy making it possible to analyze the electrophoretic motion of single particles also in concentrated and even crystallized colloidal systems [63,64]. It is clearly important to analyze what is happening with charges on colloidal particles also in systems where many particles are interacting, such as in SA, but the reason this is not yet commonplace is that the theoretical interpretation is more difficult. Most workers who studied electrophoresis at higher volume fractions have used a cell model description to analyze their results (for recent examples see Refs. [63–65]), but there is clearly room for improvements in the theory describing induced particle motion under these conditions.

An important application for which electrophoresis is intended to manipulate SA is in electrophoretic displays [66–68]. Here the motion of charged particles in electric fields is used to manipulate the optical appearance of pixels filled with particles. Electronic ink in its present most used and commercially successful form [66,67] uses the aggregation of oppositely charged and differently colored micron-sized pigment particles in the presence of an electric field to modify the grey values of each pixel.

Because opposite charge attractions combined with van der Waals forces keep the aggregated structures more or less stable even without a field and because no polarization filters are needed e-ink is significantly more power-efficient compared to other display types. An as power-efficient scheme to arrive at e-ink color screens has not yet found the market although proposed methods have appeared [68].

The ability to drive oppositely charged colloidal particles with an external electric field turned out also to be the easiest field to realize one of the simplest model systems displaying a form of pattern formation termed lane formation [50]. In lane formation particles are moved by an external field in opposite directions with strengths exceeding equilibrium forces many times. For sufficiently strong driving and high enough volume fractions systems are found to self-assemble in lanes of particles that move in the same direction. The mechanistic details of this pattern formation have by now been established both by simulation and experimental studies [50,69–71]. In short: a particle's mobility is increased in the direction perpendicular to the driving direction by collisions with particles moving in the opposite direction until on average there are only particles nearby going in the same direction. However, whether the laning transition has the appearance of a first-order-like transition or not depends on details such as the range of hydrodynamic interactions, which is different for different kinds of external driving fields, and on the dimensionality of the experiments [50,69–71]. As far as we know colloidal systems of oppositely charged particles were the first system for which this kind of pattern formation was studied quantitatively on the single particle level. However, granular particles in the form of dusty plasmas soon followed, although with less accuracy [72,73]. When the driving field is changed slightly, for instance by allowing periodic changes of direction of the driving force, the patterns formed change drastically, as discussed in the next section.

2.2 AC fields

At first hand one might perhaps not expect lanes formed in systems of oppositely charged colloids to disappear when the driving field changes direction, as the initially formed lanes will still be lanes of particles moving in the same direction. Nevertheless, this is what happens [74,75]. After several tens of cycles bands perpendicular to the driving direction form instead. This kind of bands are also seen in computer simulations [74] although 3D simulations have not yet been performed and also the role of hydrodynamics has not yet been included. It is clear from these examples that a slight change in conditions changes the pattern formation already significantly. At higher field strengths the pattern formation gets even more exotic: An oscillatory driving with spheres that have a slight difference in charge ($\sim 10\%$) display after hundreds of cycles the intriguing pattern shown in Fig. 2. The pattern formed is quite complex and dynamic and consists of strips of more concentrated particles in the driving direction next to strips of lower concentration where most of the particles are in strings [76,77]. In the concentrated strips the oppositely charged particles have separated in dynamic regions, of which the slightly charged red particles move around in swirls. Amazingly, it can be observed that both the red and green particles in the concentrated regions form extended patches of colloidal crystals at certain stages of the driving. However, when the driving stops the red and green particles mix into a liquid in which oppositely charged particles (green and red) surround each other and start to crystallize into a binary colloidal crystal. For more details about a possible mechanism see [76,77]. This kind of emergent, rich behavior is clearly hard to predict in advance and is also observed for a whole range of particle systems that are driven far out of equilibrium by external fields as reviewed in several recent papers [48–51].

In recent years there is also another related class of studies on particles far out of equilibrium that is strongly gaining in interest and level of development. These are

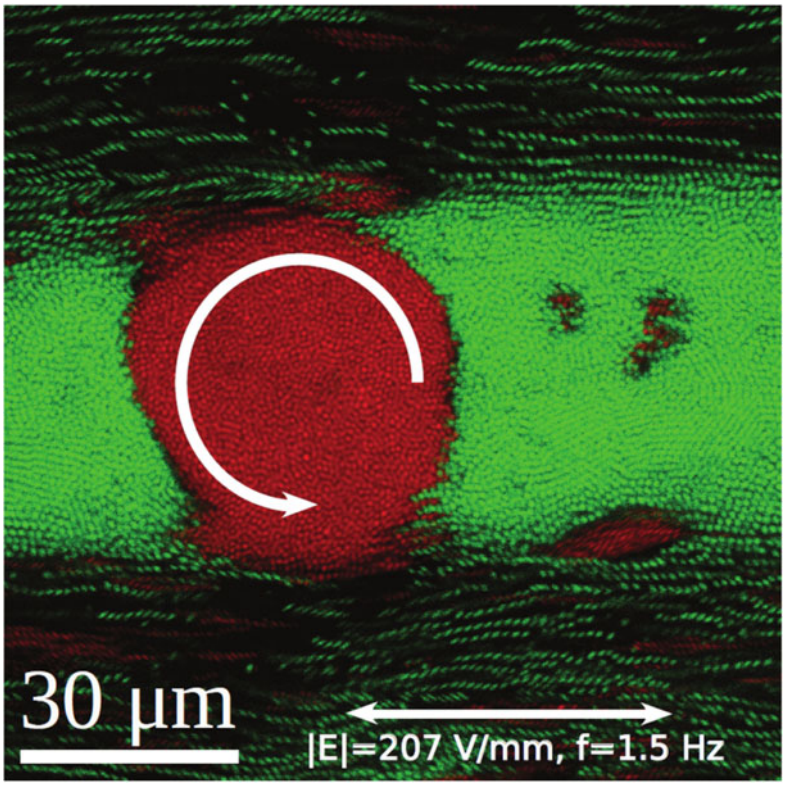

Fig. 2. Oppositely charged polymethylmethacrylate particles driven by a 1.5 Hz external electric field of 207 V/mm in the horizontal direction.

studies on so-called active matter where particles are either driven by time varying external fields, or are made to move autonomously by for instance the catalysis of a reaction on the particle surface [48]. This extra input of energy is dissipated by particle movement that is significantly enhanced compared to Brownian motion and mimics in some cases directed particle motion as used by and inside cells. External electric or magnetic fields can directly drive such swimmers, as these particles are also referred to, for instance in the case of strings of magnetic beads linked together with DNA [78] it is also possible to manipulate the swimming of this class of autonomously moving particles if for instance the direction of swimming is influenced by the field.

Finally, although the subject of electrophoretic deposition of colloidal particles onto substrates has been studied for a long time and the methodology used is actually electrophoresis, the latest developments in this field are actually to use time varying fields, to prevent e.g. electrolysis. For several reviews of these developments see Refs. [37–39].

3 Electric field induced polarizations in homogeneous fields

The study of charged and uncharged particles in time-varying electric fields in general is called electrokinetics and has, just as the use of electric fields in controlling SA, seen rapid progress [29–36]; this subject is treated also in [79–82].

Many studies performed in the past 5 decades involving both electric and magnetic fields were aimed at understanding and improving the properties of so-called

electro- (or magneto-) rheological (ER/MR) fluids [42–44]. At strong electric and magnetic fields dipolar interactions will create electrode or container spanning strings even in milliseconds for micron sized particles and the resulting jump from a low viscosity liquid to a solid with a yield stress can be used in many applications. Examples range from a variable transmission to real-time adjustable shock absorbers, or even dampeners for earthquakes [42–44]. Commercial applications have only recently come to market as conditions where there is no degradation of the ER effects is not so easy to achieve. Recent advances, although they are not fully understood, include increasing the ER response significantly, and thus also to smaller particles sizes, by using particles in combinations with liquids or coatings from molecules with a strong dipole moment. It is thought that the molecules with strong dipole moment form an oriented coating on particles, thus enhancing the ER response, see Refs. cited in [43]. Because applications in which a fast viscosity switch is achieved are the focus of this research, it is important to achieve the ER effect with as little power dissipation as possible, and thus with as small currents flowing as possible. Many other details are less important. This makes general research in ER and MR fluids not follow the different sections in this minireview too well. For instance, in some cases low currents are achieved with oils with a low dielectric constant and the frequency of the fields used is not so important. Also, as these systems are generally far out of equilibrium and also frequently involve not only electric or magnetic fields but also shear, the details of the homogeneity of the fields and the presence of field gradients are usually not distinguished or treated separately either. For these reasons ER and MR fluids and research are not mentioned in the subsequent sections, although in many cases many aspects mentioned in these sections are also relevant to this field.

3.1 Low frequency homogeneous AC fields

If the frequency of the ac electric fields is chosen to be below or around the frequency that is associated with the ions moving a distance that is comparable to the double layer thickness it also becomes possible to polarize small particles for which polarization due to a dielectric constant difference with the solvent is too weak, as this contribution is proportional to particle volume. This is possible as the double layer can for small particles significantly extend beyond the actual particle size even in water and the polarizability is proportional to volume. An example of this is the electric field induced chaining in dispersions of Au particles with a size of 30 nm in water [83]. In addition to dipolar interactions making the particles want to align head-to-to, the metallic chains connected to the electrodes result in strong and inhomogeneous field distributions close to their tips, which in turn results in strong dielectrophoretic effects as well. Dielectrophoresis is described in the next section.

Moreover, in case the induced dipoles in the double layer are not strong enough to cause significant dipolar interactions between particles compared to the thermal energy, $k_{\mathrm{B}}T$, the dipoles may still be strong enough to induce alignment of individual anisotropic particles. In addition, in ways similar to how electric fields align molecular nematic liquid crystals, collectivity in a tendency to already align can multiply small polarization induced forces of individual particles to a strong collective response to the field. A recent example of these effects in the case of colloidal liquid crystal phases is given by rod-like fd virus particles in time varying electric fields [84,85]. Thus, the electric field in this parameter regime can be used to influence the phase behavior also of colloids with a relatively small polarizable particle volume. A disadvantage is that in general the exact particle interactions become extremely complicated because of the time-dependency of the response of the ions in the many overlapping double layers surrounding the particles [86–88].

Despite the complicated nature of the inter-particle interactions as mentioned above, even for larger colloids, new and relatively simple and regular clusters can be obtained in high yield nonetheless. In a recent and promising paper it is reported that if micron sized particles are brought close to an electrode surface with ac frequencies not only in the frequency range where the ions in the double layers around the particles respond to the field, but also where the double layers being built up at the electrodes are responding, amazingly regular clusters containing just a few particles can result even with a high yield [89]! It has been long known that particles present at an electrode surface carrying a current influence the hydrodynamic flows in such a way that long-ranged attractions result [90,91]. In the paper by Ma et al. it is demonstrated that under conditions that are not yet explained in detail these long-ranged attractions, together with repulsions that also arise, amazingly regular particle clusters ($n < 6$) and their SA can be obtained [89]. Future work has to show how generic the conditions explored are for other particle systems.

Lower frequency electric or (mostly until now) magnetic fields can of course also induce dipolar interactions between particles in 2D systems where the particles are confined to a plane by walls, gravity, or a liquid interface. Because of the geometry such dipolar interactions are repulsive only, unless the field direction is not perpendicular to the plane of the particles. Particles with magnetic interactions in such systems are reviewed in another section of this special issue [92] see also Refs. cited in [48]. As far as we know electric fields have hardly been used yet to influence 2D SA.

3.2 High frequency homogeneous AC fields

There are two limits for particles with polarizable cores where homogeneous electric fields of high frequency can manipulate SA. For particles where the achievable field strengths are sufficient to significantly manipulate interparticle interactions compared to the thermal energy SA is influenced most directly. For particles that also interact through the overlap of double layers the effects of the induced polarizations within the cores of the particles can more or less be treated independently from the double layer repulsions if the frequencies of the fields used are high enough [25,93]. In addition, the for spheres to-first-approximation dipolar interactions can also be induced in uncharged particles that are index-matched at optical frequencies, because such matching of the dielectric constant at optical frequencies almost never coincides with matching at lower, e.g. MHz, frequencies. Because dipolar interactions that are the first order term in the inter particle interactions are long-ranged ($1/r^3$), the calculations and intuition to predict phase behavior are not straightforward. For two particles it is clear that a head-to-toe configuration of the induced dipoles is the lowest energy configuration and this is also the reason behind the initial formation of particle strings shortly after a field is applied. However, because of the long range of the interactions many terms need to be summed before convergence in the interactions is reached. For instance, only after a full calculation was done for the first time on this structure it became clear that a body centered tetragonal (bct) lattice of strings has a lower electrostatic energy as compared to a lattice of particle strings forming a close packed face centered cubic (fcc) lattice (see Refs. cited in [43,44]). Because there is no fundamental first principle theory for 3D phase transitions, only experiments or simulations done carefully enough that equilibrium structures result can ultimately prove that such a bct lattice indeed has the lowest free energy for hard dipolar spheres and under what kind of conditions [94,95].

Depending on the contrast difference with the solvent the induced fields are either along or opposite to the external field. It is thus possible for binary suspensions with dielectric constants both above *and* below that of the liquid to have dipolar

interactions between like spheres and *inverse* dipolar interactions between dissimilar particles. Similarly, as dipolar interactions induce chains of particles, inverse dipolar interactions tend to make the first structures that form sheet-like. This concept was cleverly explored in the binary SA of regular magnetic particle clusters in a magnetic field [96] but has yet to be explored for dielectric particles and electric fields.

If both dipolar attractions and a significant double layer repulsion are present at the same time, the region in the phase diagram where a so-called string-liquid is present is much wider compared to systems of hard dipolar particles [93,95]. Strings of spherical particles of variable stiffness were made using this fact from charged polymer particles with in addition polymer chains attached to their surfaces that acted as steric stabilizers [96–99]. By increasing the temperature while the polymer particles were forced into contact by the electric field the stabilizing polymers got attached to other particles [100] making the dipolar strings after lowering the temperature both sterically stabilized and permanent. By changing the molecular weight of the stabilizing polymer chains the stiffness of the chains of spheres could be tuned. Such strings are an interesting new (coarse grained) model system for both (semi-)flexible polymer chains and polyelectrolytes. Using binary particle systems and more complex starting particles like asymmetric dumbbells [97,98] gives even more possibilities to create more complex strings, as preliminary measurements show together with computer simulations done to better probe the enormous configuration space [99]. Although particles tens of microns in size become quite heavy in the gravitational field, a simple rotating stage may to first order eliminate the effects of gravity on e.g. SA of these strings [101].

Interactions between more complex particle shapes in homogeneous electric fields become quickly quite complicated and need to be assessed by numerical calculations and approaches such as the coupled dipole method [102,103]. For instance, it is not even that easy to infer that a single polarized cube does not align in a particular direction in a homogeneous field [102]. The more complex bowl-shaped particles shown schematically in Fig. 1b and Fig. 3 and developed in our group [104] do orient as single particles. This has been calculated with the coupled dipole method and is shown for the single particles in Figs. 3b and 3c [102]. With more particles different configurations in strings are possible. Only after alignment experiments were done on these complex shaped particles in an electric field with a strength of $\sim 10\,\mathrm{V/mm}$ (see Fig. 3) we calculated that indeed an alternating orientation, as shown on the right in Fig. 3b, has a lower interaction energy (by about $4k_\mathrm{B}T$ for two particles) as compared to the configuration on the left in Fig. 3b and explains the structures seen in the strings seen in these preliminary experiments (Fig. 3a). In the calculations a relative dielectric constant of 3 was used for the particles and 80 for the solvent.

Particles with both a convex and concave part make it possible at higher volume fraction to stack by partially fitting inside each other. This inspired us and others to design a new kind of SA that to some extent mimics what in biology is called lock-and-key interactions when particle shapes fit well inside each other. For instance, enzymes use such fits to achieve specificity in catalysis. It is clear from packing arguments that at higher volume fractions and osmotic pressures the particles will simply use the lock-and-key configuration as this increases packing fraction naturally. However, at low volume fractions such configurations can also be induced by for instance depletion induced attractions [105]. Preliminary experiments on mixtures of spherical silica particles (diameter 2.5 micrometer) with the bowl-shaped particles (with a diameter of 4 micrometer) in water in an electric field ($1\,\mathrm{MHz}$, $\sim 10\,\mathrm{V/mm}$) demonstrate that electric fields can induce such lock-and-key interactions as well. In Fig. 3c it can be seen that the spheres are drawn inside the bowls, which themselves are lined up in the field as discussed above with alternating orientations, as shown in Figs. 3a and 3b.

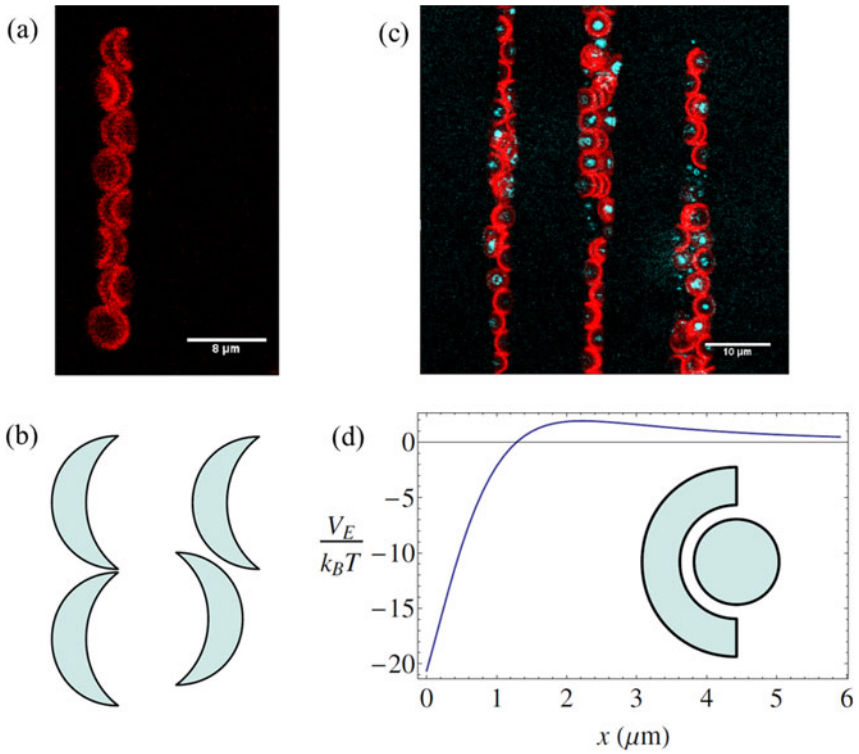

Fig. 3. (a) Bowl shaped particles (see Fig. 1a) in a homogeneous external electric field (1 MHz, 10 V/mm, scale bar 8 μm); (b) Two configurations for the coupled dipole calculations of the bowls in the same external electric field (relative dielectric constants: water: 80, bowls/silica: 3): left $-10k_BT$, right $-14k_BT$; (c) Electric-field (1 MHz, 10 V/mm) induced lock-and-key interactions between bowl-shaped particles and silica spheres (scale bar 10 μm); (d) Coupled dipole calculation showing the distance-dependent interaction potential of a sphere going into the bowl using the conditions of (c).

A coupled dipole calculation using the same dielectric contrasts as mentioned before shows with how many k_BT of binding energy the spheres are captured by the bowls at relatively low electric fields (Fig. 3d).

Finally, even when interactions in between particles are negligible a homogenous electric field can still be quite useful if its aligning effect on anisotropic particles is used. Two recent results obtained for systems of rod-like silica particles, recently developed in our group [106] illustrate this ability quite nicely: In the first example electric fields were used to switch a so-called plastic crystal where the rods were self-assembled on a 3D lattice but could freely rotate to a full crystal by aligning the rods with the field [107]. The reason these plastic crystals formed was due to double layer repulsion at least as long-ranged as the rod lengths. In experiments on similar rods, but with double layer repulsions shorter than the diameters of the rods so that the effective interactions were much more anisotropic allowing the formations of smectic liquid crystals [108] electric fields could align such smectic phases over large distance and in addition reduce also other defects [109]. At higher field strengths the induced dipolar interactions allowed the formation of para-smectic phases and two kinds of new colloidal crystal phases [109]. Similar directed SA and new crystal phases were earlier discovered for dumbbell shaped particles in homogeneous electric fields with a frequency around 1 MHz [110].

3.3 Multiple time-varying fields

We were inspired by beautiful experiments on granular magnetic particles by the Sandia group of Martin and coworkers who used up to three independently controllable, time varying magnetic fields to arrive at new interactions and structures, see e.g. Refs. [111–113]. Time varying electric fields were also set up by multiple sets of electrodes to achieve new interactions between dielectric particles [114]. An important point with these time varying fields is that for colloids on the larger side of the colloidal domain, or micrometer particles sizes, it is relatively straightforward for the electronics to be much faster than any colloidal relaxation time. This means that interesting effective time-averaged interactions could be realized by cleverly designing the functions applied to multiple sets of electrodes. An example are the already mentioned inverse dipolar interactions by using two sets of electrodes to rotationally average an ordinary dipolar interaction by fast rotation in a 2D plane. In this way an inverse dipolar interaction in the direction perpendicular to the plane of rotation results [111–115]. As already mentioned, the first structures formed by such interactions are not strings, but sheets. Such sheets are not a minimum in the energy or free energy, but can nevertheless be kinetically frozen in if the field strengths are increased fast enough [115]. If two more electrodes are added, the third field can be chosen to exactly counter the negative dipolar interactions effectively averaging the dipolar terms out in a similar way as is achieved in magic angle spinning in solid state NMR. The remaining terms in the interactions between spherical particles are proportional to $1/r^6$. This is the same distance dependence as molecular van der Waals interactions, however with subtle differences with these interactions having to do with the phases of the terms remaining [114]. It is also clear from these examples that many more complex effective interactions are still waiting to be explored using this approach both for magnetic and dielectric particles.

4 Moving particles in electric field gradients: Dielectrophoresis and electric bottles

4.1 Low frequency AC fields

As mentioned, a particle with a field induced polarization does not experience a net force in a homogeneous electric field, but only a torque. To exert a net force, which is called dielectrophoretic, one needs a gradient in the electric field. For frequencies where the double layer of the particles gets significantly polarized by conductivity of the ions surrounding them one describes the frequency dependent polarization with a complex number [45–47]. Depending on the frequency, the induced polarization can be with or against the driving field direction and the resulting motions are called positive and negative dielectrophoresis respectively. The sign and frequency dependence of the dielectrophoretic force give unique possibilities in for instance cell sorting: Because the frequency dependency of dead cells is different from that of live cells the frequency where dielectrophoresis changes sign is also different. Thus, dead and live cells can be sorted by an optimized choice of the electrode configuration and frequency choices [45–47].

4.2 High frequency AC fields

Dielectrophoretic forces which are solely due to a dielectric constant mismatch have the added benefit that they also work for un- or low-charged particles. Moreover, if

the dipoles induced are kept small enough that they do not strongly influence inter particle interactions, the field gradients will only move particles. If the gradients move particles to a region where the particles are completely contained in 3D, either by container walls and/or by other regions with electric field gradients, the concentration of particles will rise in such a confined region. This rise continues until the osmotic pressure build-up and increased particle flux opposing the dielectrophoresis balance each other. Such a 3D confined region in which the osmotic pressure and thus the volume fractions can be increased with electric field gradients was termed an electric bottle by Chaikin et al. [116]. Originally the particles were compressed by positive dielectrophoretic forces, but in a more recent extension of this technique demonstrated both for particles with hard-sphere like interactions [117] and for particles with long-ranged repulsive charge interactions [118] it was shown that for systems with negative dielectrophoresis much larger electric field gradients can be used without affecting the interparticle interactions in the middle of the electric bottle. Moreover, using an electric bottle it is possible to compress a dispersion of particles with a diameter of 3 micrometer fast enough that the compressed state is a glass [119]. Electric bottles were also already used to induce crystallization in binary dispersions [120] and in a study of classical crystal nucleation, where optical tweezers were used in addition to nucleate different crystal symmetries [61]. Especially with the new more complex colloidal model systems that are becoming available only in small quantities there are clear advantages to having the volume fraction of dispersions changed not by centrifugation but by an external electric field as this can be achieved in much smaller volumes and therefore we expect electric bottles to become an important tool to quickly probe phase behavior.

5 Combinations of electric and other fields

Electronic ink is composed of oppositely charged, micrometer sized pigment particles left to aggregate in the presence of an electric field as already mentioned, but the pixel size is determined by a polymeric shell in which this process takes place. Phase behavior depends not only on the dimension in which it takes place, but is also strongly affected by a confining geometry, which is why generally it is also considered an external field. In the e-ink application, the polymeric confining shell is essential for the working of the e-ink pixels as the van der Waals forces between the particles in the aggregates and the shell make sure an image remains for a long time even if the device is completely switched off.

In preliminary experiments we are attempting to combine the effects of confinement on the phase behavior of rod-like colloidal model particles with that of an external electric field. For an example of the confinement effects alone on silica rods dispersed in water droplets and emulsified in an oil (hexadecane) after drying of the water droplets see Fig. 4a. Similar droplets in an external electric field with a strength of about 730 V/mm (frequency 1 MHz) are shown in Fig. 4b and 4c. The complex combination of dielectric mismatches between the particles oil and water caused an unexpected effect on the particle concentration, making them go to the edge of the droplet leaving a hole in the middle that is possibly interesting for applications and that we are in the process of trying to understand in more detail.

As was already mentioned above, ER and MR fluids are used in many applications where shear is an important other external field [42–44]. However, also in applications where the aim is to stay closer to equilibrium and for instance arrive at colloidal crystals using procedures that are compatible with industrial processes like spin coating [18] electric fields can be an interesting extra field to manipulate SA. Although not much work has been done in this direction yet, early results on combining spin

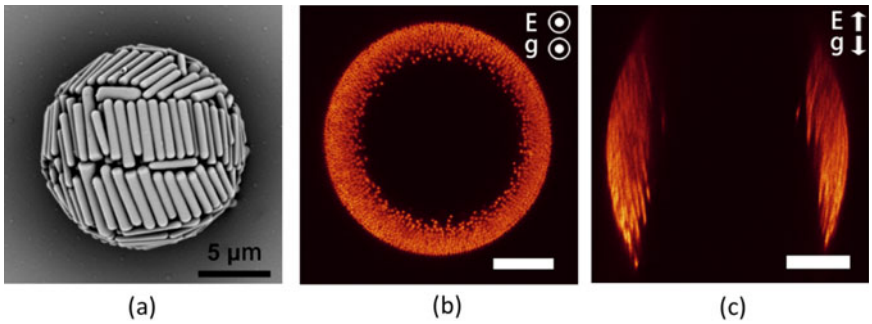

Fig. 4. Silica rods confined in water droplets in hexadecane after drying a) $L/D = 4.44\,\mu\text{m}/0.71\,\mu\text{m} = 6.25$, bar $5\,\mu$m. b,c) $L/D = 4.32\,\mu\text{m}/0.93\,\mu\text{m} = 4.65$ in an external electric field of 730 V/mm (1 MHz), bars $20\,\mu$m, b) $(x-y)$ plane perpendicular to gravity and electric field, c) $(x-z)$ plane.

coating with electric fields by Yethiraj and coworkers [121] as well as a process called controlled-drying or convective assembly by Forster *et al.* are promising [122].

6 Conclusions

The last decade and especially the last 5 years have seen ever increasing numbers of papers on the self-assembly of particles from nanoparticles to granular materials as is apparent from the many reviews covering this [2–54]. Most of this increase was driven by the development of more complex types of colloidal particles, many with a next SA step in mind. In this minireview the focus is on the use of electric fields, but in almost all cases the effects of electric fields on dielectric particles can also be obtained with magnetic particles (or there inverse: nonmagnetic particles in a magnetic fluid like a ferrofluid) and magnetic fields. Electric fields are shown to drive charged particles far out of equilibrium enabling the investigation of pattern formation on the single particle level, drive particles to swim and influence the direction of swimming, determine the gray levels in electronic ink, change particle concentrations in electric bottles, manipulate and facilitate the SA of anisotropic particles, switch plastic crystals into regular crystals, and be useful in combinations with other fields such as shear and confinement. Nevertheless, this review was far from complete, for instance not treating any optical electric field such as in optical tweezers. The examples shown, however, do make it clear that, because electric fields can influence so many aspects of colloidal particles and their SA, many new and unexpected uses and phenomena are likely to be found in the near future.

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