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Active Control of Equilibrium, Near-Equilibrium, and Far-from-Equilibrium Colloidal Systems

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The development of top-down active control over bottom-up colloidal assembly processes has the potential to produce materials, surfaces, and objects with applications in a wide range of fields spanning from computing to materials science to biomedical engineering. In this review, we summarize recent progress in the field using a taxonomy based on how active control is used to guide assembly. We find there are three distinct scenarios: (1) overcoming path-dependence to reach a desirable equilibrium state, (2) the creation of a desirable metastable, kinetically trapped, or kinetically arrested state, and (3) the creation of a desirable far-from-equilibrium state through continuous energy input. We review seminal works within this framework, provide a summary of important application areas, and present a brief introduction to the fundamental concepts of control theory that are necessary for the soft materials community to understand this literature. In addition, we outline current and potential future applications of actively-controlled colloidal systems, and we highlight important open questions and future directions.

1 Introduction

We define active control as *the application of one or more time-varying, top-down fields or forces*—including electric forces,[1,2] magnetic forces,[1–3] acoustic forces,[4–6] fluid flow,[7,8] light,[9,10] chemotactic forces,[11] thermal forces,[12] or combinations of these[13,14]—*that influence bottom-up colloidal assembly and organization processes*. The potential to actively control colloidal assembly processes has tremendous promise to create microscale structures, coatings, and bulk materials that are dynamic, responsive, and programmable, as well as provide useful solutions to difficult challenges with traditional equilibrium assembly processes. There is already a wide range of practical applications for actively controlled colloidal assembly, including metamaterial synthesis,[15–20] semiconductor fabrication,[21,22] and biological and medical innovations.[23–30] Indeed, actively controlled colloidal assemblies are a potentially paradigm-breaking technology that could enable assemblies to mimic biological systems with the ability to grow, heal, compute, move, and respond to stimuli.

Traditional approaches to colloidal self-assembly focus on bottom-up processes that approach thermodynamic equilibrium. These techniques exploit static interactions between (passive) particles to give rise to emergent structural order. There are many advantages of this approach, including inherent scalability to large numbers of colloids and an intellectual framework that allows one to "program" assembly by using thermodynamics to design particles that can assemble into desirable structures. Despite these benefits, there are drawbacks to the equilibrium approach, such as assemblies that become kinetically trapped in undesirable states, lengthy equilibration times, and inherently static structures.

Recently, bottom-up far-from-equilibrium self-organization processes have received significant attention. These processes exploit continuous energy inputs (e.g., with "active" particles[31–36]) to create organized structures that cannot be completely described using equilibrium thermodynamics.[37–39] There is significant enthusiasm about such systems, as it is believed that biological materials grow and differentiate via far-from-equilibrium processes,[40] suggesting that they have a vast and under-exploited potential. An additional advantage over equilibrium assembly processes is their ability to exhibit dynamic behavior. However, non-equilibrium processes complicate the design and practical execution of creating colloidal structures compared to equilibrium methods. In particular, non-equilibrium systems experience *degeneracy* and *path-dependence*, where a single initial state can reach different final configurations via a time-dependent process. This latter property makes non-equilibrium systems more difficult to "program" and control.

Active control of colloidal assembly is an alternative paradigm that proposes the use of *top-down* methods to control bottom-up equilibrium self-assembly and non-equilibrium self-organization processes.[2,10,41,42] Active control has the potential to both im-

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prove self-assembly and self-organization processes and to provide assemblies with novel properties that are not possible without external control. For example, active control may be used to optimize equilibrium assembly processes that are slow to equilibrate or become kinetically trapped. One recent demonstration of this principle used time-varying (active) inputs of electric and magnetic fields to drive time-dependent particle interactions and form defect-free crystals.[43–45]

There are perhaps yet greater possibilities for controlling nonequilibrium self-organization processes. These processes contain degeneracy and path-dependence that complicate the dynamics, but in turn these properties provide degrees of freedom that can be readily manipulated using top-down control. Recent examples exploiting these properties have led to rotating microgears,[9] reconfigurable microrobot swarms,[46] and "living crystals" that continuously break apart and reform.[47] Accordingly, the marriage of time-varying top-down manipulation with bottom-up assembly processes is a powerful combination that potentially leads to *scalable, real-time control of self-assembly and self-organization processes*.

Despite the promising progress, much work remains to realize the full potential of adaptable, time-varying, or intelligent structures, surfaces, and materials. To aid in further progress, we provide a critical review of the field with a focus on creating a taxonomy that identifies the way in which active control is being used to direct self-assembly or self-organization processes. In particular, we focus on three conceptually distinct situations where active control is being used:

(I) System manipulation to achieve a desirable *equilibrium* result by either changing the location of the energy minimum or escaping unwanted metastable states;

(II) Creation of a desirable *metastable, kinetically trapped*, or *kinetically arrested* result by manipulating the shape of the energy landscape;

(III) Creation of a desirable *far-from-equilibrium* result through continuous energy input.

As shown in Figure 1, these situations are neatly summarized by their relationship to the near-equilibrium concept of a kinetic path on a free energy landscape.[48,49] In situation (I) active control is used to change the position of the global minimum of the free energy landscape to consistently reach a specific final state (Figure 1a), or help the system more efficiently and consistently reach the global minimum of the free energy landscape (Figure 1b). The situation shown in Figure 1b is applicable when slow kinetics prevent the system from reaching a desired equilibrium state within an experimentally accessible timescale.

In situation (II), shown in Figure 1c, control methods are used to alter the kinetic path to trap the system at a desirable local minimum in the free energy landscape. This is often seen in path-dependent processes where multiple metastable states exist. The desired states can be achieved either through a specific kinetic path, such as different thermal processing times, or—if undesirable metastable states are long-lived compared to the desired one—by supplying extra energy to escape the arrested states.

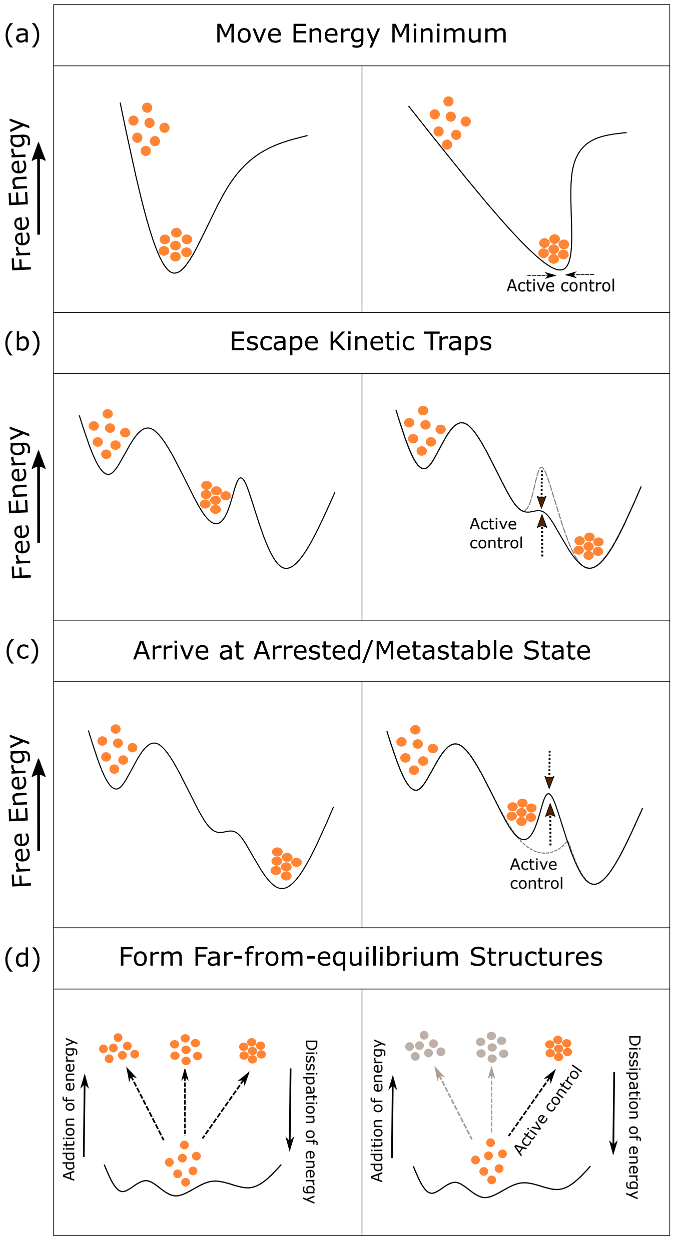

Fig. 1 Distinct scenarios where active control is used to direct self-assembly and self-organization processes categorized by their relationship to a hypothetical free energy landscape. (a) Active control that moves the energy minimum. (b) Active control changes the energy landscape to arrive at equilibrium more quickly or with fewer defects. (c) Active control that changes the energy landscape to create a useful near-equilibrium structure. (d) Active control that selects one of several possible far-from-equilibrium results.

Situation (III) is far-from-equilibrium, and the free energy landscape no longer drives the system dynamics. Instead, as pictured in Figure 1d, external energy inputs permit dissipative processes to reach one of several possible steady states that are not necessarily an energy minimum. Active control techniques can be used to (1) bias the system towards a certain configuration, or (2) guide the transition between different configurations.

In this review, we do not attempt to comprehensively survey every paper that uses active control to assemble colloids. Instead, we have selected examples using many top-down fields and forces that will most clearly demonstrate to the soft matter community the advantages of using active control. In addition to the review we present here, there are several recent, excellent reviews that discuss active control of colloidal assembly and organization processes with different emphases. Tang and Grover[50] focus on the sensors, actuators, and control methods used for guiding colloidal self-assembly. Harraq et al.[1] and Liljestrom et al.[2] focus on the use of electric and magnetic fields to control assembly, and Van Ravensteijn et al.[11] review the use of chemical reactions to make non-equilibrium states.

Finally, it is important to note that as an emerging field, nomenclature is sometimes a source of confusion, and at the outset we seek to clarify a few concepts and terms. The time-varying and (frequently) non-equilibrium nature of “active control” distinguishes it from the more limited paradigm of “directed self-assembly”,[42] which employs an unchanging template, field, or force to alter the equilibrium state of assembly. Additionally, in contrast to some others,[1] we include externally-controlled fields in our definition of the thermodynamic system, meaning a system with a non-zero applied field can reach equilibrium. That is to say, when the field is changed, the system must come to a new equilibrium that is different from the no-field equilibrium. We prefer the term “far-from-equilibrium assembly” to the term “dynamic self-assembly” for self-organization processes that require continuous energy input.[2,37,40] Instead, we reserve the word “dynamic” for systems that are physically moving, which includes many but not all far-from-equilibrium results. While “programmable” assembly is not the main focus of the review, its definition is often ambiguous in the literature. We use it to denote cases where user-supplied information (either contained within the material or supplied by top-down methods) are used to achieve a desired state.[51] Finally, we typically refer to equilibrium and near-equilibrium processes as “self-assembly” and far-from-equilibrium processes as “self-organization.”[52]

With the above in mind, the review is organized as follows. We discuss specific challenges to achieving active control of colloidal materials, and we review techniques that have been used to overcome them in Section 2. In Section 3, we discuss Approach (I), namely using active control to create a desired equilibrium result, and in Sections 4 and 5, we discuss Approaches (II) and (III), respectively. In Section 6, we discuss some of the possible applications of colloidal system with active control. Finally, in Section 7, we conclude with a discussion of the open questions and possible future directions for the field.

2 Challenges and solutions to applying active control to colloids

The fundamental challenge to imposing top-down control on bottom-up processes is the mismatch between length scales and system sizes (i.e., number of colloidal particles in the system) between the two approaches. Top-down techniques use externally controlled fields and forces to assemble individual materials and objects. For example, laser-based optical tweezers are used to position micron- or sub-micron-scale objects such as cells or silica beads relative to one another.[53,54] Top-down techniques are versatile and precise, but alone they cannot reach all length scales of interest in a way that can be scaled to fabricate microscopic structures.[41] Bottom-up techniques deal with a complimentary set of length scales (< 100 nm), but they do not have the same versatility and precision as top-down methods.[41]

This fundamental reality translates into a number of specific challenges when attempting to control the self-assembly or self-organization of colloids. These include a general lack of real-time sensors, stochastic nonlinear dynamics, high dimensionality, unintentional kinetic trapping, a lack of local actuators that leads to underactuation, and, finally, a large design space that is difficult to explore systematically.[55] Sensors, which include different types of microscopes, are expensive and may not be available for real-time measurements.[50] Nonlinear dynamics make control difficult because slight changes to parameters may cause abrupt changes to the behavior of a system, and stochastic dynamics make precision and consistency difficult to achieve. Colloidal systems are high-dimensional when each particle is treated independently, and this makes them difficult and expensive to model without reducing the dimensionality of the system. Particles may also get stuck in unintentional kinetic traps, which are hard to characterize and model. Local actuators (meaning top-down influences that affect only a subset of the particles) for colloidal systems are rare and limited, and macroscopic global variables such as temperature and composition may disrupt particles that have already assembled. Finally, the design space of possible combinations of building blocks, interactions, and top-down inputs to apply is large and very difficult to explore systematically to generate useful results.

To solve these problems, researchers have used a combination of techniques to measure, model, and manipulate colloids, including (i) feedback control, (ii) model-based control, (iii) dimensionality reduction, and (iv) inverse design. In contrast to open-loop control where a pre-designed control program is used without any further measurements, *feedback control* refers to any control method where measurements (e.g., positions of colloidal particles) are used to make calculated adjustments to control inputs (e.g., top-down field to apply) that will guide the system to a desired final state (e.g., high degree of crystallinity). Feedback control can deal with the stochastic dynamics and kinetic traps that are inherent to colloidal systems. In *model-based control*, a dynamic model relates the control inputs to the measured values. Such model-based control strategies handle the nonlinear dynamics and underactuation present in colloidal systems. However, a dynamic model that treats each measured particle position independently becomes unmanageably complex. To deal with the "curse of dimensionality", *dimensionality reduction techniques* such as order parameters and machine learning may be used. Finally, identifying a result that can be achieved using the control strategies previously mentioned is a difficult task in itself. Recent *"inverse design" principles*, which use constrained optimization to explore the design space and discover desirable results, have been proposed as a solution to this problem.

In the remainder of this section, we review the basic principles of (i)-(iv) that are relevant to colloidal assembly. Examples of the techniques mentioned in this section will appear throughout the rest of this review. One purpose of this section is to make it easier for the reader to grasp these techniques so they may be applied to new systems to create increasingly useful applications in either equilibrium, near-equilibrium, and far-from-equilibrium assembly processes.

2.1 Feedback and open-loop control

Control operations can be either open-loop, where a predesigned control program is used without any measurements needed, or closed-loop/feedback controlled, where measurements (position, velocity, temperature, etc.) are used to guide assembly to a desired final state. Open-loop strategies are typically used when sensors are unavailable or expensive.[56,57] However, they perform poorly when knowledge of the system is incomplete or imperfect, such as for the stochastic dynamics of colloidal self-assembly.

Feedback control can be used when sensors are available and is generally more stable and robust than open-loop control. This is important for colloidal systems because inherently stochastic dynamics mean repeated experiments can produce different results even in the absence of noise.[55] Historically, feedback control has not been used to direct assembly at the length scale of colloids, but recent advances in sensing and computation have allowed feedback control to become a possibility.[50] Accordingly, feedback control has been used in equilibrium self-assembly to escape unwanted kinetic traps.[45,58] It has also been used in far-from equilibrium systems of active particles to mimic the group formation and cohesion of biological systems.[59,60]

2.2 Model-free and model-based control

The nonlinear dynamics and underactuation present in colloidal systems can be addressed using one of two general types of controllers: model-free or model-based. Model-free controllers are simpler to implement, but they do not perform as well and rely on the existence of established heuristics. Model-based approaches do not require preestablished heuristics to derive a control law, but they are more complicated to produce, and in some cases they rely on an online optimization step that is too slow to implement in real time. This subsection is divided into three parts. First we will discuss how model-free and model-based approaches deal with the problems of nonlinear dynamics and underactuation. Then we will present three models used in model-based control of colloidal systems. Finally, we will discuss two approaches to implementing a controller in real time.

Nonlinear dynamics and underactuation are present in nearly all colloidal systems.[55] Nonlinear dynamics are difficult to control because slight changes to parameters may cause extreme changes to the behavior of a system. Standard control strategies are derived by assuming they will be used on a linear or linearized system, and so basic control techniques may not perform well on highly nonlinear systems.[61] Underactuation, which refers to the inability to control the motion of individual particles, is also a problem in colloidal systems. Since local actuators (or inputs that influence only a subset of particles) are rare, control algorithms must be written in terms of global properties such as temperature and composition. Changing these global variables may disrupt particles that have already assembled. To deal with nonlinear dynamics and underactuation, a controller may take one of two forms: model-free or model-based.

The most well-known model-free control method is proportional-integral-derivative (PID) control.[61] A PID controller is a feedback controller that uses proportional, integral, and derivative functions of the error, or difference between the measured value of a variable and desired value of that variable, to calculate control inputs to apply. PID control has been used in several cases to guide equilibrium colloidal systems.[44,62,63] For example, Gao and Lakerveld[62] implemented a PID controller that used dielectrophoresis to control the density of colloidal particles in a microfluidic device. In this example the nonlinear dynamics were dealt with using gain scheduling, where the PID gains changed depending on the magnitude of the error. Underactuation was dealt with using the heuristic that a stronger field produced a higher density. When such heuristics can be discovered, a PID controller with gain scheduling may be effective. However, when such heuristics do not exist, a different approach such as model-based control must be used.

Both the complicated nonlinear dynamics and the underactuation present in colloidal systems can be dealt with using model-based control.[64] Model-based control deals with the nonlinear dynamics by explicitly modeling them, for example by using a force balance on individual particles. The dynamic model may be physical, empirical, or data-driven (e.g., machine learning). The dynamic model, written in terms of the global variables used as inputs, is used to predict how a given input would affect the future state of the system, and this information is incorporated into the control algorithm. Optimization or machine learning is used to discover the optimal control policy without having to rely on human-supplied heuristics.[65]

Model-based strategies have already been used for controlling equilibrium self-assembly,[12,57,66–69] or identifying and avoiding unwanted kinetic traps.[57,70] Model-based controllers may be open-loop (i.e., they may not require real-time measurements), or they may take advantage of feedback to improve consistency and precision. In the following paragraphs we will introduce several models that are commonly used, including Langevin equations, Master equations, and machine learning models.

Langevin equations describe stochastic motion in continuous systems.[71] They are derived from Newton's equation of motion where the only forces affecting a particle are the drag force and a random fluid force from solvent molecules.[55] Models based on Langevin equations have been used to direct continuous processes such as colloidal crystal assembly.[12,67–69]

Systems with a discrete number of possible states are modeled by Master equations. A Master equation, also called a Markov state model, is a set of differential equations that model the probabilities of each state the system could occupy.[72] The probabilities are often calculated by averaging over many simulations.[55] Master equations are well-suited for systems where the number of states is small, such as modeling the number of crystals in a droplet,[66] or when the configuration space can be divided into discrete sections.[45] However, when the number of states becomes large, Master equations become computationally intractable.[12,56]

In addition to physical models, both discrete and continuous processes may be modeled using machine learning. Machine learning is useful when large data sets exist for training. However, models based on machine learning may give results that are difficult to accurately interpret. Machine learning has been used to model both equilibrium[73–76] and non-equilibrium[48,77] assembly. A review of applying machine learning to soft materials engineering, including colloidal self-assembly, is given by Ferguson.[78]

Applying model-based control to colloidal assembly creates a new problem: the controller may be too slow to perform in real time. For example, this has occurred in research using model predictive control.[45,79] This drawback can be overcome using dynamic programming. Dynamic programming is a technique in which the optimal control problem is broken into smaller subproblems. The solution to each sub-problem can then be stored and used to reduce the computation time for future calls to the controller.[79] Dynamic programming has been used to speed up the control of colloidal assembly by computing the control policy offline and implementing it as a look-up table that is quickly accessed in real time.[45]

Finally, instead of creating a dynamic model and implementing it using dynamic programming, the modeling step can be skipped completely using a machine learning technique called reinforcement learning. Reinforcement learning is not model-based control as described above because it does not model the dynamics of a system. However, it accomplishes the same purpose as model-based control by relating the state of a system to the optimal control inputs. In reinforcement learning, the control policy is learned directly from the experiment by using trial and error to maximize a reward function. Reinforcement learning has been used to find the optimal control policy to guide crystal formation using an electric field[12,80,81] and in simulations to guide patchy particles to assemble into a particular polymorph.[82] Reinforcement learning does not require the derivation of a dynamic model, which is useful if the dynamics are difficult to model or if the dynamics drift over time.[45] However, the drawback is that a controller that uses reinforcement learning takes large amounts of data to train.

2.3 Dimensionality reduction

Modeling and controlling self-assembly are difficult when the measured data is high-dimensional. For example, a colloidal crystal is composed of thousands of individual particles whose positions can be tracked by a visual sensor. Individually controlling the motion of each of the colloidal particles would be extremely difficult. Instead, control algorithms have been made to track aggregate variables formed from the position data, such as the degree of crystallinity.[12,44,69,80] In other words, information from the high-dimensional data is condensed into a tractably small set of parameters that describe the phenomenon of interest. Aggregate variables can be identified using physically meaningful order parameters and/or using empirical descriptors identified by machine learning.

Order parameters are a concept from thermodynamics used to characterize phase transitions, where a physically measurable variable goes from zero in one phase to nonzero in another. Order parameters are often used to characterize phase transitions in simulations,[83] and they have also been used to guide the creation of colloidal crystals in studies where the individual colloids were large enough to be tracked by microscopy.[44,49,80] Stochastic models such as Langevin-based models and Master equations can be modified to model how the order parameters change with time.[69,80] For example, two common order parameters are the radius of gyration to identify condensed phases and the number of hexagonally close packed neighbors to capture degree of crystallinity.[12,44,49,69,80]

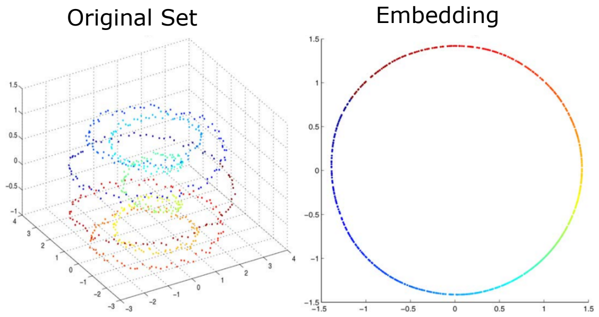

Fig. 2 A diffusion map is used to embed data collected in a noisy helix pattern in three dimensions (left), where the changing color represents the passing of time, into a two-dimensional space (right). Adapted from Reference 84 with permission from Elsevier.

Machine learning can also be used to reduce the dimensionality of data without relying on physically measurable variables. Many machine learning techniques exist, including linear methods, such as principal component analysis, and nonlinear methods, such as manifold learning.[76,78,85] In colloidal assembly the current state-of-the-art technique for reducing high-dimensional data is a nonlinear technique called a diffusion map,[12,48,69,78,86,87] illustrated in Figure 2. A diffusion map is a technique introduced by Coifman and Lafon[84] to embed high-dimensional data onto a low-dimensional geometric space. The embeddings are computed using eigenvectors and eigenvalues of a diffusion operator on the data, and when only the largest eigenvalues are used, the data can be described using a reduced number of dimensions. For example, in Figure 2, the original three-dimensional data is plotted on the left, with color representing time, and the same data embedded into a diffusion map of only two dimensions is plotted on the right. The largest eigenvalues of the diffusion operator are empirical descriptors that can be used as convenient aggregate variables. In some situations it is possible to relate the empirical descriptors identified by a diffusion map to physically meaningful order parameters,[12,69,75] but this is not always possible.[75] Diffusion maps have been used to guide both equilibrium self-assembly[12,69] and non-equilibrium self-organization[48,86] processes.

2.4 Forward and inverse design

In forward design, a researcher creates building blocks, observes them organize into a structure, and then measures the properties of the resulting structure. By synthesizing many different results, a researcher may identify heuristics for creating structures with desirable properties. However, the design space for potential structures is immense and slow to explore systematically. Adding time-varying active control adds another dimension to the forward design space, making it even larger.

By contrast, in inverse design,[74,77,88–94] a researcher specifies desirable properties, then uses optimization algorithms[89,90,92] and machine learning[74,77] to identify the structure and building blocks that will produce those properties. Inverse design greatly speeds up the discovery of useful structures. However, the inverse problem is generally much more difficult to solve than the forward problem.

Recent reviews of inverse design strategies have been given by Sherman et al.[88] and by Dijkstra and Luijten.[74] In general, inverse design involves identifying a figure of merit, then using constrained optimization to navigate the design space of possible colloidal systems and determining the building blocks, interactions, and combination of external inputs that will score the highest on that figure of merit. This requires a model of the design space, which is currently lacking for many non-equilibrium processes. However, new non-equilibrium theories, methods, and models are quickly being developed.[77,89,92,95,96]

3 Controlled equilibrium systems

In this section, we review approaches to control equilibrium self-assembly. Recall that we choose to include externally-controlled fields in our definition of the thermodynamic system. That is to say, when an external field is applied, the system will come to a new equilibrium that is different from the no-field equilibrium. Any sudden change to a system, including the application of a top-down input, temporarily drives a system away from equilibrium. In this section, we consider cases where this input is used to produce an equilibrium (minimum free energy) configuration.

Accordingly, we consider here cases where an external fields is applied for one of the two reasons: (1) to actively modify the energy minimum to follow a changing set-point (Figure 1a), or (2) to escape kinetics traps/kinetic arrest and arrive at equilibrium (i.e., the global minimum in free energy) faster (Figure 1b). A good example of the former is the use of external fields to modulate structural color in dynamic color-change materials.[97–99] An example of the latter is escaping kinetic traps by using temperature or electric/magnetic fields to produce defect-free crystals.[45]

3.1 Active manipulation of the equilibrium state

Active control of an external field can be used to manipulate the free energy minimum of a system. This is because an energy landscape may be a function of global parameters, such as temperature and electric/magnetic fields, and changing these parameters moves the energy minimum to create a new equilibrium state. Active control may be used to switch a material between two distinct phases, potentially providing a mechanism for reconfigurable materials[100] or actuation in soft robotics.[101] Alternatively, active control may be used to actively tune the properties of a material, which could be used for dynamic metamaterials applications such as adaptive camouflage.

The simplest case is to use top-down control to switch a colloidal system between two phases. For example, a system may be switched from a disordered fluid to an ordered crystalline phase using temperature,[83,100] pH,[102] voltage,[103,104] light,[105] or acoustic waves.[39] Top-down control has also been used to switch between crystal structures with different optical properties,[106] between glasses and crystals,[107] and between a disordered fluid and microtubes.[108] The control method in these examples is a simple open-loop on/off switching. One could argue that with such a simple control law, these systems may be classified as directed self-assembly without active control. Indeed, this is reasonable, and we see the traditional paradigm of directed self-assembly as the base case of active control. More advanced systems, such as reconfigurable materials, will build on this base case and require active control beyond simple on/off switching.[100]

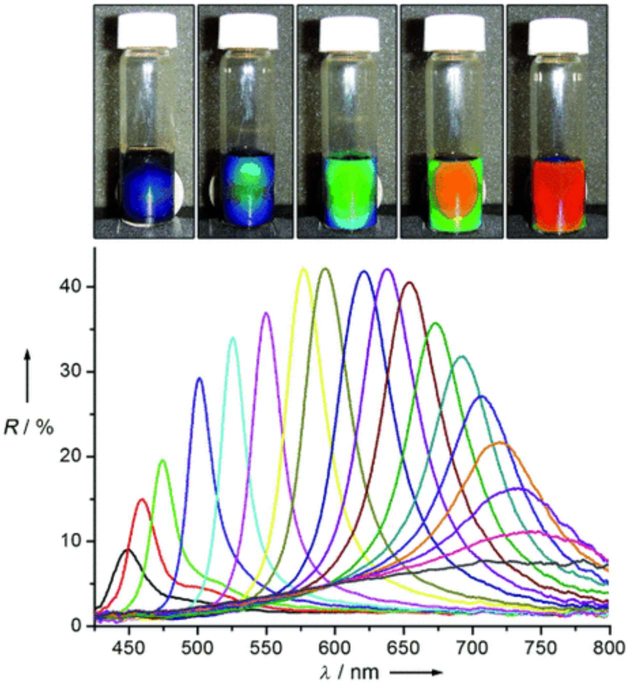

Fig. 3 Superparamagnetic crystals of colloidal magnetite changed color as a permanent magnet was moved closer (right to left). The diffraction peaks of the crystals are also shown as the distance from the magnet was decreased (right to left) from 3.7 to 2.0 cm with a step size of 0.1 cm. Adapted from Reference 97 with permission from Wiley.

Model-free open-loop control beyond simple on/off switching has also been used to dynamically tune the optical properties of colloidal materials.[97–99,109] The classic example of a material with dynamically tunable properties was given by Ge et al.[97] and is shown in Figure 3. Ge et al. tuned the band gap of photonic crystals made of superparamagnetic colloidal magnetite by changing the strength of a magnetic field. Applying the magnetic field made the magnetite particles self-assemble into crystals. As the strength of the applied magnetic field was increased, the equilibrium lattice spacing of the crystals decreased, and this changed the reflection spectra of the crystals so that the color of the mixture shifted from red to blue, as shown in the top panel of Figure 3. This color change was also completely reversible. More broadly, structural color change is an ongoing active area of research,[110] and so far it has only required open-loop control. This is because crystals are typically large enough that defects created by the stochasticity of colloids do not significantly affect the optical properties. We anticipate that future color-change materials that exploit smaller-scale crystals may require more advanced control methods. If so, feedback control is an attractive solution because color changes can be sensed without a microscope.

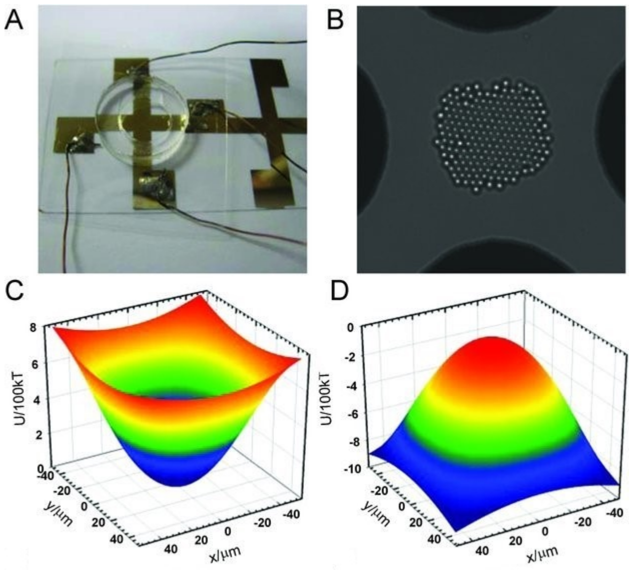

Fig. 4 A quadrupole electrode patterned on a microscope slide (a) created an AC electric field that caused silica particles to assemble into a crystal (b). A frequency of 1MHz created an energy maximum in the center (c), while a frequency of 0.1MHz created an energy minimum in the center (d) and caused a controlled disassembly of the crystal. Adapted from Reference 44 with permission from Wiley.

Feedback control has been applied to manipulate the equilibrium state of a colloidal assembly for other applications using a microscope as a sensor and electrodes as the control inputs. The first example of feedback-controlled colloidal self-assembly was created by Juarez and Bevan,[44] who used an electric field to create a two-dimensional crystal, as shown in Figure 4. They used microelectrodes patterned onto a microscope slide (Figure 4a) to create an alternating current (AC) electric field and manipulate silica particles suspended in fluid. When the AC field was turned on at a high frequency of 1 MHz, particles moved toward the center of the four electrodes (Figure 4b) due to a potential energy minimum (Figure 4c) created by the electric field. A digital camera and optical microscope tracked particle positions to compute an order parameter representing the degree of crystallinity. Using the heuristic that a higher field strength increased the value of the order parameter, a proportional feedback controller was constructed to move the order parameter to a set point by changing the voltage of the field. Furthermore, the authors demonstrated the ability to partially disassemble the crystal by lowering the frequency of the AC field to 0.1 MHz and create an energy maximum (Figure 4d), which could be used to repair defects through partial disassembly and reassembly. More examples of switching between fields to create better crystals and further innovations on this system will be given in the following section.

In addition to the above examples of global actuation, researchers have also developed *local actuators* using light,[105] fluid flows,[8,111] and electric fields[56,62,63] to create precisely defined colloidal structures. For example, an algorithm was designed by Solis et al.[112,113] to place time-varying point charges to control the positioning of nanoparticles. This method was later adapted to use AC electrodes and implemented experimentally by Gao and Lakerveld[63] to create lines of particles, as shown in Figure 5. Using electrodes made of indium tin oxide (ITO) patterned with photoresist stripes, silica particles were directed into a line. With a series of steps in which the voltage and frequency of the electrodes were modulated with time, the electric field moved the particles onto the photoresist stripes, and PI feedback control was used to ensure that the lines were only one particle thick. In further work, they first improved their methods by implementing a gain-scheduling PID controller[62] and then a model-based open-loop controller.[56] The latter method is particularly effective, because it eliminates the need for experimentally laborious real-time observation. Their control methods proved to be successful for aligning colloidal silica particles, but there are challenges in scaling such methods with local actuators to larger numbers of particles. This drawback, as well as the fact that few methods of local actuation have been developed, means that assembly using local actuators has not yet been widely explored.

Of the scenarios outlined in Figure 1, active manipulation of the equilibrium state is likely the most mature approach. Much of the literature is an extension of concepts from directed self-assembly and uses global actuation with relatively simple control methods such as on/off or PID control. As noted, there are some examples of local actuation and (open-loop) model-based control, but the focus on manipulating the equilibrium landscape makes it unlikely that these approaches will play a large role. Instead, promising avenues for future research may lie in greater use of feedback control. For example, several authors have suggested that feedback control could potentially be used to fabricate metamaterials with dynamically tunable properties.[44,68,114,115]

3.2 Faster and defect-free equilibrium states

Perfect crystals or otherwise defect-free equilibrium states are often necessary for creating desirable materials, such as metamaterials with the novel properties mentioned in other sections.[45,116]

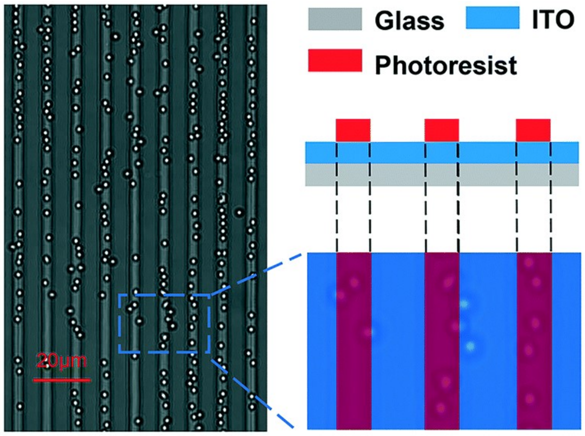

Fig. 5 Silica particles were aligned using AC electrodes made of ITO and patterned with stripes of photoresist. A feedback controller was used to change the electrode voltage and frequency to move the silica particles onto the photoresist stripes in a defect-free line. Adapted from Reference 63 with permission.

However, during the process of equilibration, it is easy to get kinetically trapped in an imperfect or disordered arrangement of particles. Top-down control can be used to bypass kinetic bottlenecks and avoid common metastable phases to quickly reach defect-free equilibrium phases, including those that are sometimes otherwise unreachable. We focus here on cases that reach equilibrium; studies that used active control to *arrest at a desirable metastable state* will be discussed in the following section.

Defect-free equilibrium states have traditionally been made using an open-loop control process called annealing. Thermal annealing is a process where a crystalline solid is heated to a specified temperature and then allowed to cool slowly. This gives defects and internal stresses the energy to escape kinetically trapped states and relax to equilibrium.[117] Other types of annealing also exist in soft matter systems. For example, in solvent annealing a solvent is added and then slowly evaporated off. Similar to thermal annealing, the solvent allows the system to overcome energy barriers and escape disordered metastable states.[118]

Like annealing, open-loop cycling of external fields has been used to avoid kinetic arrest in colloidal crystals.[119–123] Swan et al.[119] studied paramagnetic latex particles that formed chains that aggregated laterally and kinetically arrested in a steady magnetic field. However, toggling the magnetic field on and off at the correct frequency caused the chains to escape the kinetically arrested state and arrive at an equilibrium crystal state that was otherwise inaccessible. This and other simple open-loop control cases[120–123] illustrate the point that top-down control can be used to reach defect-free equilibrium states by leveraging alternate dynamic pathways.

In cases where open-loop control is insufficient, feedback control can be used to give more precise and consistent results. For example, model-based feedback control was used to improve the micropatterned electrode system for assembling SiO_2 particles into 2D crystals that was introduced in the previous section (see Figure 4).[67,68,80] As before, defect-free crystals were created by imposing an electric field, but in Ref. 68 Tang et al. show that switching electrodes between different voltages modifies the energy landscape and enables the system to avoid kinetic traps. The Master equation-based controller was implemented with dynamic programming to drive the system rapidly to a high degree of crystallinity with a 98% success rate compared to a 60% success rate for uncontrolled crystallization (defined as the number of crystals that achieved perfect ordering in 1000 seconds, see also Ref. 80 for related simulations).

These feedback control methods worked well for 2D crystals with relatively small numbers of particles. While possible, it takes more sophisticated methods to track individual particles and similarly manipulate a 3D system. Instead, feedback control can be used in conjunction with sensors that track aggregate variables (e.g., order parameters) that are easier to observe. For example, Griffin et al.[73] used crystal mass and the number of crystals as aggregate variables to control molecular crystallization using temperature. A similar strategy could potentially be applied to 3D colloid crystallization if better sensors are developed to track order parameters without the need to directly measure the positions of individual particles.

In summary, open-loop, feedback, model-free, and model-based control have all been used to guide equilibrium colloidal assembly. Open-loop control is an option when sensors are not available or prohibitively expensive. When sensors are available, feedback control provides increased consistency and precision to the final result. Model-free control works well when heuristics can be used to relate global variables such as temperature or magnetic field to the behavior of the system. Model-based control does not require the use of human-created heuristics, but it is difficult to implement on new systems. One of the challenges for applying the model-based control methodology given in the previous examples to new systems is that it can be difficult to construct a model, even when basing it on Langevin equations or Master equations. In these situations, if plentiful data is available, machine learning can be used to construct the dynamic model.[45]

4 Near-equilibrium systems

As mentioned previously, a system can be trapped in a local minimum of the free energy landscape due to a sufficiently large energy barrier.[83,124,125] In this situation, the system is *kinetically trapped* in a metastable state. It is also possible that—although it is not in an energy minimum—the kinetics are slow enough that a system stays in an arrested state within any reasonable experimental timescale, as may occur with colloidal glasses and gels. We refer to a system in this situation as being in a *kinetically arrested state*. Together, metastable and kinetically arrested states may be categorized as “near-equilibrium” states because they can be understood using equilibrium concepts such as free energy landscapes.

In practice, it can be difficult to distinguish if a physical system is trapped in an energy barrier or is simply in a region of kinetic arrest. Thus we will instead organize our discussion around two other interesting features of both types of near-equilibrium systems: path-dependence and degeneracy. Path-dependence means that because the system fails to reach equilibrium, the properties of a colloidal assembly depend on the processing history to which the system is subjected. From an energy landscape perspective, this means that (even for a fixed landscape) processing can be used to place a system in a local energy minimum[124] or to lead a system through a region of kinetic arrest.[126] Degeneracy implies that multiple persistent configurations exist, and that it is possible to switch between them. Usually, degeneracy occurs when there is a "rough" energy landscape with multiple metastable states of similar free energy. In the following subsections we provide examples of how active control can exploit degeneracy and path-dependence to achieve useful non-equilibrium states.

4.1 Process history dependence

A desired non-equilibrium configuration can be created by carefully controlling its processing history. The most common way to process a colloidal assembly is through quenching or annealing, where temperature (or another global state parameter) is used to navigate the energy landscape to either pass by or to kinetically arrest in a state of interest.[116,117] Alternatively, if several local free energy minima are possible, external fields or forces may be used during processing to change the free energy landscape with time to direct the system towards a targeted energy minimum.[57]

Colloidal glasses and gels are two well-known examples of near-equilibrium systems that are created by controlling processing history.[127,128] Both glasses and gels exhibit path-dependence. For example, a glass—a kinetically-arrested state—can be formed by rapidly changing the temperature, whereas a more gradual temperature change can lead to crystal formation even though the final temperature can be the same in both cases. In the jargon of control theory, quenching is one of the simplest examples of model-free open-loop control. While the use of more complex control techniques may be important in the future, so far, the use of active control to achieve metastable/kinetically arrested states has mostly been open-loop and empirically driven, as seen in the following examples.

One area of recent interest has been an investigation beyond traditional single-step temperature quenches to more complex multi-step thermal profiles.[126,129–132] This strategy has been used to make gels that are more resistant to aging,[129] to create hierarchically structured materials,[130] and to synthesize multicomponent gels with applications in photonics and drug delivery.[126] In one illustrative example, Di Michele et al.[126] subjected gel-forming DNA-coated colloids to a two-step temperature profile with an intermediate temperature of variable length before a final quench. They found that the two-step procedure led to a different gel microstructure than the traditional single-step quench, and that varying the holding time of the intermediate temperature led to materials with tunable properties. Cheng et al.[129] used a similar two-step temperature profile on a nanoemulsion gel and found that it was more resistant to aging. Immink et al.[131] also investigated multi-step temperature profiles of a thermoresponsive microgel made of two different types of particles (i.e., a binary microgel or bigel). As shown in the confocal micrographs in Fig. 6, the microstructures of these bigels are also sensitive to their thermal history. Immink et al. found that a slow, two-step temperature profile (Fig. 6a) produced a "core-shell" gel structure with a single-component scaffold onto which the second component condensed. By contrast, faster quenches (Fig. 6b-c) resulted in a gel without the core-shell structure and with a thinner network mesh. The gels also differed significantly in their mechanical properties.

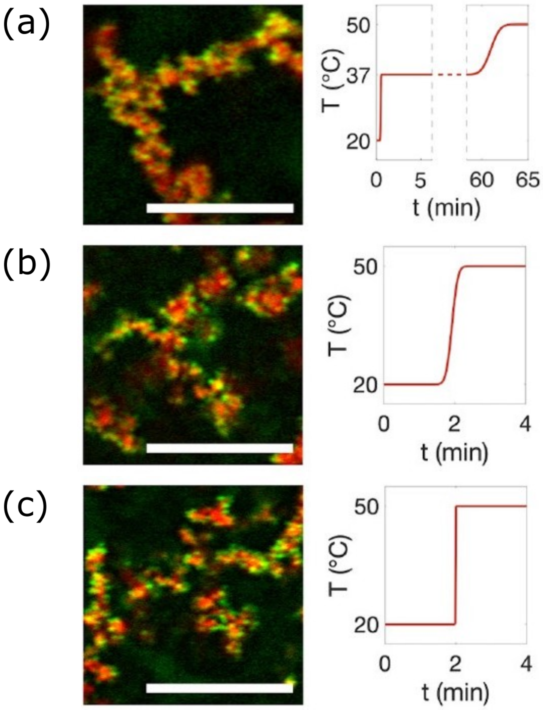

Fig. 6 A binary microgel composed of a mixture of cross-linked poly-N-isopropylacrylamide (pNIPAm) particles and poly-N-isopropylmethacrylamide (pNIPMAm) particles that forms different microstructures depending on the temperature history. In part (a), the mixture was held at an intermediate temperature and heated very slowly (60 minutes); in part (b) the temperature was heated quickly (2 minutes), and in part (c) the temperature change was near instantaneous. Additional experimental details are found in Ref. 131. Adapted from Ref. 131 under an ACS AuthorChoice License.

Toggling schemes have also been used to achieve path-dependent near-equilibrium structures. In Section 3, we discussed how toggling a magnetic field on and off at a given frequency can be used to approach the equilibrium state more quickly.[121] In further simulation and experimental work, Sherman and Swan,[121,122] and Kim et al.[123] showed that toggling fields can also be used to access and stabilize metastable states. Note that persistent toggling is a form of continuous energy input, technically making this a case of far-from-equilibrium assembly. However, Sherman and Swan showed that if instantaneous quantities are replaced by their time averages, the behavior can be explained using concepts from near-equilibrium thermodynamics.[121,122]

In Ref. 121, Sherman and Swan performed simulations in which interparticle attractions (a proxy for a magnetic field) were toggled on and off at different frequencies. In Figure 7, they show that (i) metastable phases that are short-lived in a steady field can become long-lived in a toggled field, and (ii) that field-toggling can be used to control the final state. Principle (i) is demonstrated in the bottom right panel of Figure 7 where a metastable liquid-liquid coexistence becomes long-lived when the toggling frequency is low. Switching to a higher frequency, the system crystallizes (top right and top left), which is a lower free-energy state. The system remains crystallized when the frequency is lowered again (bottom left), demonstrating principle (ii). Sherman and Swan[122] later extended their simulation work to show stabilization of additional crystal structures. Finally, Kim et al.[123] performed experiments mirroring the system of Sherman and Swan. They used a toggled magnetic field to extend the phase diagram to include more nonequilibrium states, and they demonstrated experimentally that a toggled field can be used to consistently arrive at different near-equilibrium states by taking advantage of different kinetic pathways.

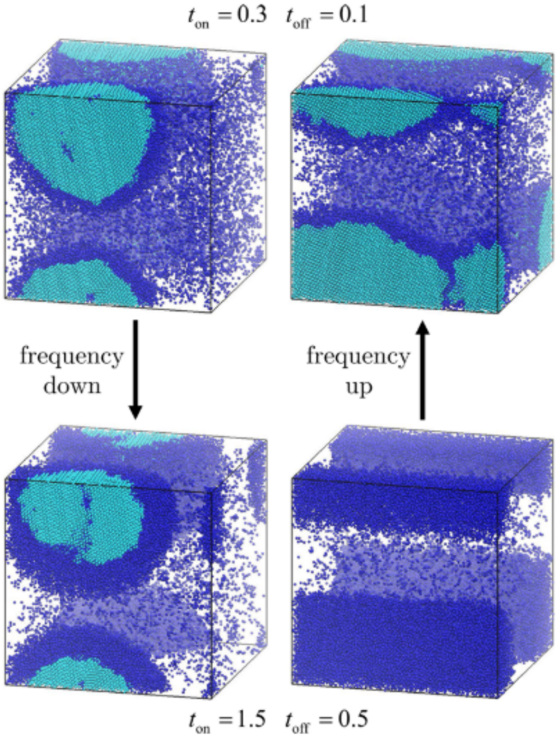

Fig. 7 Simulations of colloidal assembly in a toggled magnetic field demonstrating pathway dependence. Liquid-liquid coexistence is observed at low-frequency (bottom right). When the frequency is increased (top-right and then top-left) the system crystallizes. When the frequency is subsequently decreased (bottom-left), the system remains crystalline. Reprinted with permission from Ref. 121. Copyright 2016 American Chemical Society.

In principle, more complex control methods such as feedback control can also be used to create a desired non-equilibrium state. For example, in the previous section we discussed how feedback can be used to avoid kinetic traps.[58] Several authors have suggested that the reverse is also possible: feedback control can be used to modify the energy landscape to ensure that the system arrives at a desired kinetically trapped state.[45,133] However, to the best of our knowledge, to date this idea remains untested in colloidal systems.

4.2 Switching between multiple end-states

In some systems with multiple energy minima, it is possible to use active control to reversibly switch between states. Alternatively, if the energy barrier is low enough that the system switches spontaneously, active control can be used to raise the energy barrier to trap the system in one of the states. A non-colloids example of switching between multiple end-states is the well-established technology of phase-change materials, which were used, for example, in the 1990s to create re-writable optical disks.[134] These phase-change materials used heat-quench cycles around the glass transition to create crystalline and glassy bits on the disk to record information. A similar principle can also be applied to switchable colloidal materials.[135]

Active control can be used to modify the energy landscape of a system to switch between metastable states. An example of a switchable colloidal optical material was given by Stratford et al.[136] They performed simulations of colloidal particles mixed with liquid crystals that formed multiple metastable states that could be switched between using a magnetic or electric field. Switching between metastable states with different optical properties could be used for applications such as e-paper. Another example of a colloidal material with switchable states was given by Bharti et al.[14] Using particles that were subject to both a magnetic field and an AC electric field, they created metastable intermediates (networks, bidirectional chains, and 2D crystals) that led to the formation of networks with different properties. Bharti et al. conclude that their strategy of using multiple types of fields is useful for controlling the density and stiffness of colloidal gels, which could lead to materials with adaptive properties.

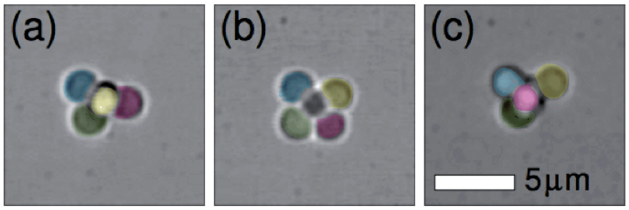

Fig. 8 Spontaneous switching between two configurations of a digital colloid tetramer. Reconfigurable digital colloids have been suggested as a method of memory storage in unusual computing environments. Reprinted from Reference 137, with permission.

Active control can also be used to raise an energy barrier to trap a system so that it cannot switch spontaneously. One particularly interesting example of this principle are “digital colloids” that were created by Phillips et al.[137] Digital colloids are colloidal clusters that can switch between discrete microstates due to thermal fluctuations, with the possibility to use external control to “lock” the state in place. They have potential applications as high-density information storage or computing elements.[137] The simplest example is a chiral tetrahedral structure made of five colloidal particles, shown in Figure 8. This structure was observed to switch from one chiral configuration to its mirror image, as illustrated from left to right on the figure, thus acting as a binary material capable of storing one bit of information. These two states are energetically equivalent, but the energy barrier between them is low enough that spontaneous switching can occur. Phillips et al.[137] suggested that an external control such as an electric field, change in temperature, or change in solvent concentration could be used to raise the energy barrier and lock the structure in place.

Due to the nature of switchable states, simple open-loop control techniques such as on/off switching and step-wise tuning are likely all that is required to produce and switch between the states. However, model-based approaches can give insights into discovering new metastable states through inverse design.[77,89] For example, Nguyen and Vaikuntanathan made a general model that relates a given non-equilibrium configuration of particles to the chemical potential of the monomers that will produce it. This type of model could be used as a starting place to designing processes that will produce a desired kinetically trapped structure.[95]

5 Far-from-equilibrium systems

In far-from-equilibrium systems, continuous energy input and dissipation allows particles to self-organize into ordered states that may be either stationary or dynamic. Note that dynamic assemblies are a unique attribute of far-from-equilibrium systems that are not possible in the previous categories. Far-from-equilibrium systems have potential applications as responsive materials,[47] nano/micromachines,[9,10] and they offer opportunities for researching and understanding the mechanisms behind biological swarms and other biomimetic technologies.[11,46]

By definition, far-from-equilibrium systems cannot be fully described by thermodynamic concepts such as a free energy landscape, which makes it difficult to control such systems using approaches developed for equilibrium or near-equilibrium processes. To date, general theories of far-from-equilibrium assembly are an extremely active area of research, but there has yet to be a consensus on the best approach.[95,138,139] The lack of general theories makes applying model-based control to far-from-equilibrium systems challenging, and so far, most of the control techniques that have been applied to these systems have been open-loop and empirically determined. However, one can say at least two things. First, while it may be possible to define a (time-dependent) energy landscape, doing so does not give useful insight into the organized state of the system. Indeed, one may take this observation as a distinguishing feature of a far-from-equilibrium process. Second, similar to near-equilibrium systems, far-from-equilibrium colloidal assemblies also exhibit path-dependence and degeneracy. Accordingly, as before, actively controlling external forces that vary in both space and time can be used to achieve a desired stationary or dynamic state. Additionally, active control can be used to switch between two or more states that exist at different values of an external field.

5.1 Processing history dependence

In a situation similar to kinetic trapping, far-from-equilibrium systems can also be caught in a specific final state that depends on their processing history. This is accomplished using spatially- or temporally-varying external fields or forces. In one particularly interesting manifestation of this phenomenon, top-down locally-applied forces are used to assemble far-from-equilibrium micromachines that persist even after the top-down forces are removed.[9,10] Thus, even though multiple configurations are possible, processing leaves the structure “trapped" so that it is unable to switch to a different configuration.

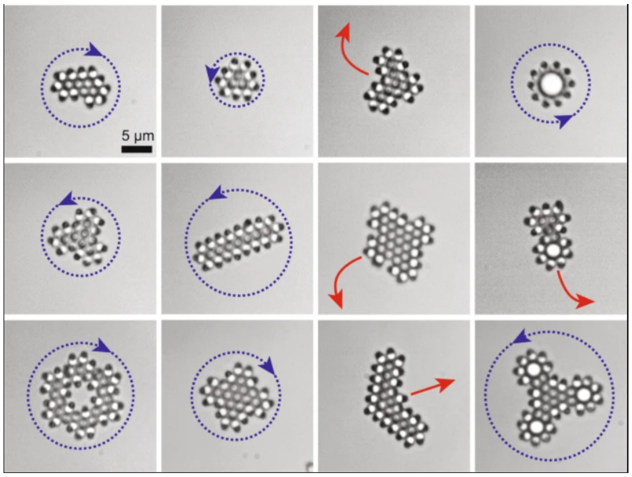

Fig. 9 Micromachines assembled from Janus particles made of a photoactive hematite cube attached to an inert polymer bead. Optical traps focused on an area caused beads to assemble into a structure that depended on the optical trap template and that persisted even after the lasers were turned off. First column: chiral machines rotate in a fixed direction. Second column: centrosymmetric machines rotate by spontaneous symmetry breaking. Third column: axisymmetric machines have translational motion. Fourth column: hybrid machines have the active particles assemble around passive spheres. Adapted with permission from Ref. 10 under a CC BY 4.0 license.

A specific example of using local actuation to create history dependence in a far-from-equilibrium system was given by Aubret et al.[9,10] and is shown in Figure 9. They used Janus particles, made of photoactive hematite cubes attached to inert polymer beads, that were activated under illumination. When uniformly illuminated, the particles exhibited random, self-propelled motion that is expected for active Janus particles. However, when a laser was focused on an area, a group of seven particles self-assembled into a rotating microgear.[9] The microgear persisted with a speed of rotation determined by the light intensity even after the laser was turned off as long as there was uniform light illumination. Notice the interaction between active control and history dependence; temporary laser illumination directed assembly towards a stable and steady microgear state rather than active Brownian motion or other more complex states.

This work was extended beyond microgears in Ref. 10 to include more complex micromachines using different optical trap (laser) patterns, as shown in Figure 9. Micromachines included chiral and centrosymmetric machines that rotated in a fixed direction, axisymmetric machines with translational motion, and hybrid machines made from a combination of active and passive particles. As with the microgears, these micromachines were assembled from active particles that were uniformly illuminated. When a templated pattern of optical traps was shined on a region of particles, they assembled into a micromachine dictated by the optical template which persisted even after the optical traps were turned off. However, when a new optical trap template was applied, the micromachines reorganized into a different shape.

These findings suggest that highly controllable time-dependent dynamics are possible, and they point towards the possibility of developing shape-shifting materials.

Another example of history dependence was given by Grotsch et al.[140] They used gold and iron oxide nanoparticles functionalized with DNA that assembled when an organic fuel was present. In these experiments, adding a large amount of fuel all at once produced a kinetically trapped assembly that did not disassemble for several weeks. However, adding the same amount of fuel in smaller quantities over time produced a temporary structure that persisted when the fuel was present, but fell apart once the fuel was depleted. Similar to the previous example, this experiment reiterates the principle that self-organization of a far-from-equilibrium system is not necessarily reversible, even when the external energy source or fuel is removed. This is an important point to keep in mind when designing a controller for situations in which it is desirable to switch between multiple far-from-equilibrium states, as discussed in the following section.

Far-from-equilibrium self-assembly already offers a huge field of possibilities, and applying active control broadens the field even more. Because the results of active control and path history are not always intuitive, we postulate that inverse design algorithms that use optimization and machine learning to navigate the design space more effectively could greatly accelerate the discovery of interesting far-from-equilibrium results. Inverse design principles have been applied to non-equilibrium self-assembly in situations where modeling strategies exist,[77,89,93] but new theories and models must be developed for far-from-equilibrium systems before these strategies will reach their full potential.

5.2 Switching between far-from-equilibrium states

Analogous to the scenario in Section 3 on equilibrium assembly, far-from-equilibrium systems may self-organize into different configurations depending on the external field applied. Active control may then be used to switch between these configurations.

There are several examples in the literature where external fields and forces have been used to switch far-from-equilibrium colloidal systems between different modes of behavior.[46,141–145] Zhang et al.[145] investigated how Quincke rollers formed different patterns in different on and off pulse times, including flocks, clusters, vortices, and lattices with different lattice constants. Xie et al.[46] studied a swarm of magnetic colloidal particles that created different formations by adjusting the direction and frequency of a rotating magnetic field. The formations included an evenly distributed "liquid", a line of particles called a “chain", an aggregated swarm called a “vortex", and synchronized lines or “ribbons". Yan et al.[141] examined the behavior of Janus spheres, silica half-coated in a metal, that assembled in an alternating current (AC) electric field. As shown in Figure 10, switching the field frequency led to different configurations including swarms, chains, and clusters. As we detail below, this type of switchable behavior could be used to create microrobots, for example as agents for drug delivery.

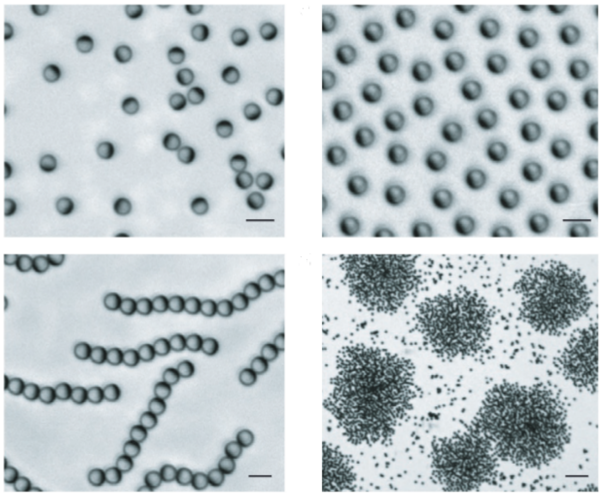

Fig. 10 Janus spheres assembled into different configurations as the frequency of an AC field is varied. The states were labeled gas, swarms, chains, and clusters. Adapted with permission from Reference 141. Copyright 2016 Springer Nature.

External fields or forces may also be used to control chemical reactions kinetics in a way that allows a system to switch between far-from-equilibrium states.[47,142,146] An example of this was demonstrated by Singh et al.[146] and is illustrated in Figure 11. They studied a binary system composed of passive particles and Janus particles that self-propelled by decomposing hydrogen peroxide when irradiated with UV light. By themselves, the active particles did not cluster, but when passive particles were included in the system, the light-activated Janus particles formed a nucleus that the passive particles clustered around, as shown in Figure 11. The intensity of the UV light affected the photochemically driven reaction rate and controlled the strength of interaction between the active and passive particles. Thus, increasing the intensity of the light allowed each Janus particle to add an additional layer of passive particles around it. Interestingly, Singh et al. also played with particle geometry, showing that particle clusters with hexagonal symmetry led to ordered lattices whereas particles that led to pentagonal symmetry formed a glass. Particles giving clusters with square symmetry were sensitive to light intensity, with low intensity generating an ordered lattice but high intensity leading to glass-like disorder.

The above are all examples of model-free open-loop control, but more advanced control techniques are also applicable to far-from-equilibrium systems. In simulations, Norton et al.[147] used model-based optimal control to calculate control inputs to switch an active nematic liquid between a clockwise and a counterclockwise rotating state. The control inputs were an applied stress that could be produced by light and an applied rotation rate that does not have an experimental analogue. Although their controller cannot yet be reproduced physically, their methods show that model-based optimal control can be applied to far-from-equilibrium in situations where a dynamic model for the system exists. However, to apply model-based approaches to far-from-equilibrium systems more broadly, new tools must be developed to model non-equilibrium systems.

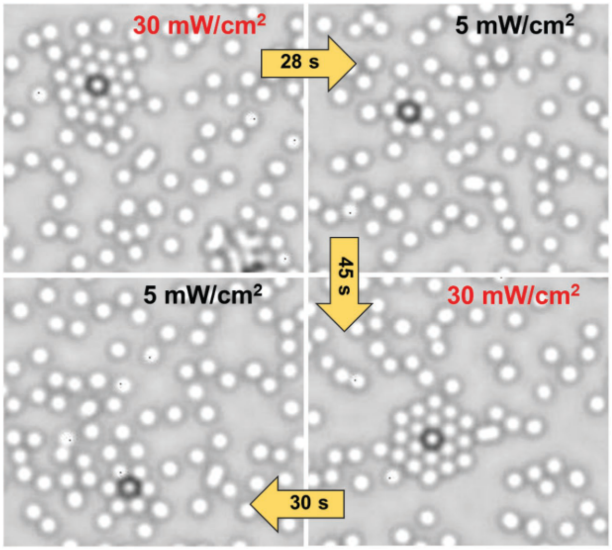

Fig. 11 Clusters of passive particles form around self-propelled Janus particles when light is on. The number of layers that formed around each Janus particle depended on the light intensity and was completely reversible. Reproduced from Reference 146 with permission from Wiley.

6 Applications of actively controlled colloidal systems

Active control of the assembly of colloidal systems have a wide range of potential applications. In this section, we specifically highlight the fields of photonic materials,[15–20] drug delivery,[25–29] and smart materials.[86,137] A running theme in these applications is the way in which active control addresses challenges to colloidal assembly. We underscore three notable themes that appear below. First, the movement of colloids is largely dominated by Brownian motion, which makes it difficult to precisely and consistently create useful and functional assemblies. Second, many assemblies are much more useful if they are defect-free or optimized in some other way that is hard to achieve using bottom-up forces alone. Finally, numerous applications require colloidal assemblies that are dynamic or adaptive to their environment. As discussed in Section 2 and seen in the examples below, active control will be invaluable for addressing these challenges.

6.1 Photonic materials

One application of colloidal self-assembly is the creation of photonic materials, which are periodic structures with a band gap that blocks a certain frequency range of light. For example, photonic crystals give butterfly wings their color and iridescence, as shown in Figure 12.[148–150] Photonic crystals have applications for coatings on lenses and mirrors,[17–19] color-changing paints and inks,[17–19] miniaturization of semiconductors,[21,22] solar-cell coatings,[12] and optical computing.[12] Many photonics applications require defect-free colloidal crystals of a consistent size. Active control strategies have been used to create such defect-free crystals with a high degree of consistency.[45]

Active control may also be used to create photonic materials with color-changing properties. Chameleons change color by actively tuning the lattice spacing of photonic crystals in their cells. This gives them advantages in social signaling, camouflage, and potentially passive thermal protection,[151] which suggests the possibility of developing these capabilities in synthetic materials.[2] Active top-down control could be used to direct how the photonic properties of colloidal crystals change with time to produce applications such as adaptive camouflage, smart glass, and e-paper.[136]

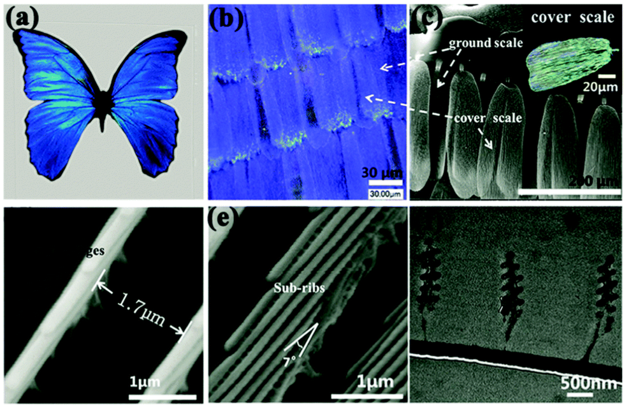

Fig. 12 Butterfly wings naturally covered in photonic crystals. The microstructure of the scales reflects wavelengths that create the irridescent blue color of the wings. Adapted from References 148 and 149 with permission.

Another useful photonic material is a negative-index material, which has potential applications in super-resolution imaging and cloaking devices.[20] In general, such materials require structural elements smaller than the wavelength of light and arranged in a way that gives the material both a negative electric permittivity and a negative magnetic permeability, which is difficult to achieve at optical wavelengths. Several different negative-index metamaterials have been produced,[152–157] but the technology is still in its infancy and further research is required to scale up sizes and improve transmission. Active control can be used to manipulate the permittivity and permeability of a material by changing its structure to explore new candidates for negative-index materials more quickly. It can also be used to ensure perfect isotropic crystals to improve transmission.[68]

6.2 Drug delivery

Traditional drug delivery routes, such as pills, lotions, or injections have the advantage of simple administration and good patient compliance.[158] However, there are also two disadvantages that we wish to highlight. First, some drugs have low solubility in water and low intestinal resorption, which means their efficacy is reduced by the time they reach targeted sites.[158] Second, the drugs may be toxic to non-targeted sites. Targeted drug delivery approaches can maximize the efficacy of the drug and minimize toxicity to non-targeted sites.[158,159] Colloidal particles have been proposed as agents for drug delivery, and targeted drug delivery contains two stages that would potentially benefit from active control: site-targeting transport of the drug carrier and release of pharmaceutical agents after reaching the destination.[25–27,159] The following examples illustrate the potential benefits of using actively controlled dynamic colloids to aid drug delivery.

Site-targeting transport of the drug carrier is important for minimizing the area exposed to potentially harmful drugs. However, the locomotion of colloid-sized objects is a non-trivial research topic that has been studied for decades.[160–162] Transport of colloids within biological organisms is even more complicated due to the complexity of biological environments. For instance, different tissues and patients under different conditions might have different requirements for drug dosage and distribution,[163] and the delivery pathways may exhibit confinements of different geometries.[164]

It has been suggested that these challenges can be met using an adaptable swarm of colloidal particles as drug-delivery agents. As shown in Figure 13, controllable adaptable swarms are possible. As discussed above, Xie et al.[46] has demonstrated swarming magnetic colloidal particles with controllable formations including “liquids”, “chains”, “ribbons”, and a “vortex.” Such a reconfigurable swarm of particles could be useful for drug delivery applications by adapting to the different environments present in the human body. For example, the vortex could be used to carry heavy loads, the ribbons could be used to cover large areas in a synchronized manner, and the chain configuration could be used to pass through narrow spaces such as blood vessels.

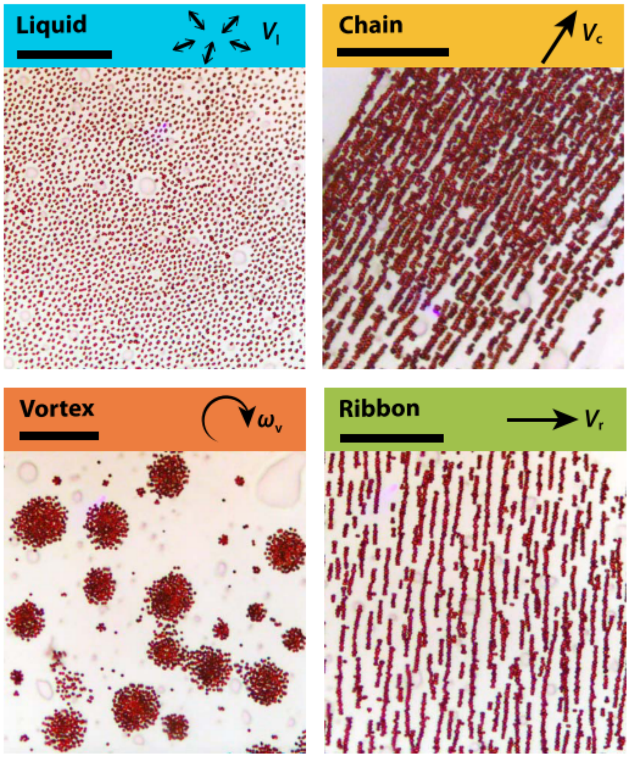

Fig. 13 Peanut-shaped magnetic colloids change formations in different rotating magnetic fields. Such a reconfigurable swarm has been suggested as an agent for drug delivery. Adapted from Reference 46 with permission from AAAS.

The second challenge of targeted drug delivery is implementing controlled release. Controlled release of drugs after the drug delivery agents reach their destination could maximize the efficacy as well as minimize the adverse effects of therapy.[158,159] Responsive surfactants have been suggested as ideal materials for soft medical microrobots due to their ability to change shape and size in response to external stimuli, which also makes them ideal candidates as actively controlled systems.[165,166] Take responsive hydrogel colloids as an example, where hydrogels can fold and unfold for targeted delivery in response to temperature or light.[167] Active control of temperature or light can be used to change the folding behavior of hydrogels, i.e. the size of openings in the folded structure, to achieve controlled release of drugs when delivered to the targeted sites. The same concept can also be applied to responsive swelling/unswelling,[168,169] or ultrasound induced shape change,[170,171] to enable the controlled release of loaded molecules.

6.3 Smart materials

It has been suggested that in the future, colloidal materials could be designed to respond adaptively and intelligently to their environment through cooperative feedback.[142,172] These types of smart materials are highly desirable for self-healing,[173] self-regulation,[174] sensors,[175] or anti-counterfeiting.[175] To a lesser extent, any material that reacts to external inputs in a controllable and reversible way may also be called a smart material.

Researchers have put much effort into designing smart materials where the material itself performs numerical computations. This paradigm of “materials that compute" interprets the programmable response of these materials to external stimulation as a logic input.[176] Thus chemistry and biochemistry are used to create analogues for logical variables, which are connected through network to function as logical circuits, thus performing computation. The logical variables can be represented by the conditions of the material, such as pH, electrostatic interactions, molecular weight distribution, volumetric variations, etc.[176–179] One interesting proposal of such a computing material that uses colloidal particles is the “digital colloids” introduced in Section 4.2.[86,137] Digital colloids are colloidal clusters that can switch between multiple configurations, and active control is needed to set and lock/unlock the configuration. Such materials may be useful as a form of high-density reconfigurable memory storage that can eventually be used for soft robots and other unconventional computing environments.

Self-healing materials have also attracted considerable attention as a class of smart materials. Self-healing materials are inspired by biological systems with the capability to recover from damages with minimal interference. Self-healing has been demonstrated using polymer healing agents to cover damaged sections of the material[180–184] or using molecular crystals that recover their previous shape after irradiation or thermal treatment.[185,186] Recently, self-healing colloidal crystals have also been demonstrated in literature.[187–191] Many of these recent examples use colloids either bonded to polymers or embedded in a polymer matrix. Lee et al.[190] presented DNA-crosslinked colloids that deform when dehydrated and then recover their original crystal structure when rehydrated. Ma et al.[189] demonstrated photonic crystals crosslinked by a polymer that perfectly healed when cut. Yin et al. et al.[187] made a self-healing photonic crystal by using a magnetic field to embed colloids into a hydrogel structure. Active control could be applied to each of these cases to help study or improve the results. For example, control principles could be used to create a crystal with the desired photonic or material properties inside the polymer structure before curing. Or, inverse design principles could be used to discover colloid-polymer systems with the required properties for self-healing.

Finally, self-healing is also present in far-from-equilibrium systems. Massana-Cid et al.[188] showed how crystals made of magnetic colloidal rotors healed when the magnetic field was increased, as shown in Figure 14. The colloidal rotors assembled into into a two-dimensional carpet when a magnetic field was applied. When they increased the amplitude of the field, defects in the carpet were repaired in a process similar to annealing.

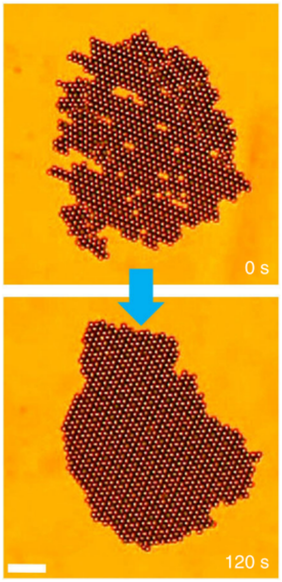

Fig. 14 Crystals made of magnetic colloidal rotors quickly transitioned from a defective/polycrystalline state to a single crystal when the amplitude of the magnetic field was increased. Reproduced from Reference 188 under a Creative Commons CC BY license.

7 Open questions and future directions

Active control may be used to modify the equilibrium state of a system, modify the energy landscape to create an organized near-equilibrium state, or to select a preferred far-from-equilibrium state for a system. It also offers the possibility of tuning fields and forces to make more precise and consistent materials and to control the dynamic properties of materials. As such, active control is a promising avenue for creating new materials with useful properties for many fields of science and engineering, especially in the areas of photonics, drug delivery, and smart materials.

However, there are problems that remain unsolved, including high dimensionality, unintentional kinetic trapping, the need to model complicated dynamics, and a lack of sensors and actuators to provide feedback. Future research will need to solve these problems with both instrumental innovations, such as the development of new sensors, and with methodological solutions, such as the development and application of active control techniques that include feedback control, model-based control, and dimensionality reduction.

Feedback control has only recently been applied to equilibrium self-assembly because of advances in the available sensors. So far, very few examples exist of using feedback control to produce a non-equilibrium result. Currently, far-from-equilibrium assembly mostly employs microscopes to directly image the configuration of particles. Certainly, reduced costs and increased quality have made optical microscopy increasingly accessible and useful. However, future innovation in sensor technology aimed at indirect measurements, such as measuring the photonic properties of aggregates instead of individually imaging the particles, will be important for increased use of feedback control in a wider range of situations.

Another reason more complex control methods are not applied is the uncertainty over what variables should be measured and controlled or what to use as a reference state. This uncertainty often stems from high dimensionality, and machine learning is a good candidate method that can be applied to identify a reduced set of dimensions. Diffusion maps are another promising method that has already seen wide use as a dimensionality reduction technique in colloidal systems. We expect that diffusion mapping and other nonlinear dimensionality reduction techniques will play an important role for the future of actively-controlled assembly.

A related but different way of addressing the high dimensionality of colloidal systems is to design particles with internal feedback—that is each particle contains internal control elements that respond to its local environment to direct self-assembly towards a desired result. This concept is related to the field of consensus control of multi-agent systems.[192–194] It is possible that results from the field of consensus control could be portable to active top-down assembly, enabling rapid progress on designing process for materials that assemble using internal feedback.

Model-based control and reinforcement learning are more obvious "low-hanging fruits" and can be applied more broadly. For example, model predictive control shows promise for guiding a system to a desirable near-equilibrium (kinetically trapped) state, and model-based control using machine learning is especially promising for near-equilibrium self-assembly.[78] However, simple models based on standard thermodynamics do not generally provide insight into far-from-equilibrium systems, making these systems more difficult.[89] Perhaps techniques such as reinforcement learning and genetic algorithms could be used to identify and guide the creation of desirable far-from-equilibrium states, as it has been done in equilibrium and near-equilibrium self-assembly.[73,76,92,195]

Another promising research direction is to use optimization[89,90] and machine learning[74,77] to reverse-engineer desired structures by discovering "inverse design" principles that will create a given desired state.[91,92] Non-equilibrium self-assembly already offers a huge parameter space for exploring behavior, and active control techniques further expand the scope. As such, inverse design algorithms could greatly accelerate the discovery of interesting non-equilibrium results, especially since the results of active control and path history are not always intuitive.

The future is bright, and opportunities abound in the field of actively-controlled colloidal assembly. All of the research areas surveyed here contain important and tractable fundamental and applied questions, and active control may be the missing key to enable viable applications for many areas of colloidal assembly. In addition, improvements and enhancements to the development of equipment, tools, and methods for active control in any one area will inevitably carry over to other fields, further enabling advancements in the field. Along these lines, we hope that this review contributes to a unified framework and interpretation of the literature on the self-assembly of colloidal systems and the way in which active control is applied. Clearly, this field is of interest to many but remains in its infancy, and we anticipate an explosion of consequential and beneficial research in the years to come.

Conflicts of interest

There are no conflicts of interest to declare

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Notes and references

1 A. A. Harraq, B. D. Choudhury and B. Bharti, *Langmuir*, 2022, **38**, 3001–3016.

2 V. Liljeström, C. Chen, P. Dommersnes, J. O. Fossum and A. H. Gröschel, *Curr. Opin. Colloid Interface Sci.*, 2019, **40**, 25–41.

3 A. Spatafora-Salazar, D. M. Lobmeyer, L. H. Cunha, K. Joshi and S. L. Biswal, *Soft Matter*, 2021, **17**, 1120–1155.

4 Z. Li, H. Zhang, D. Wang, C. Gao, M. Sun, Z. Wu and Q. He, *Angew. Chem. Int. Ed.*, 2020, **59**, 19884–19888.

5 C. E. Owens, C. W. Shields, D. F. Cruz, P. Charbonneau and G. P. López, *Soft Matter*, 2016, **12**, 717–728.

6 M. Akella and J. J. Juárez, *ACS Omega*, 2018, **3**, 1425–1436.

7 K. Zhao and T. G. Mason, *Rep. Prog. Phys.*, 2018, **81**, 126601.

8 F. Martínez-Pedrero and P. Tierno, *J. Colloid Interface Sci.*, 2018, **519**, 296–311.

9 A. Aubret, M. Youssef, S. Sacanna and J. Palacci, *Nat. Phys.*, 2018, **14**, 1114–1118.

10 A. Aubret, Q. Martinet and J. Palacci, *Nat. Commun.*, 2021, **12**, 6398.

11 B. G. Van Ravensteijn, I. K. Voets, W. K. Kegel and R. Eelkema, *Langmuir*, 2020, **36**, 10639–10656.

12 M. A. Bevan, D. M. Ford, M. A. Grover, B. Shapiro, D. Maroudas, Y. Yang, R. Thyagarajan, X. Tang and R. M. Sehgal, *J. Process Control*, 2015, **27**, 64–75.

13 Y. Yang, A. T. Pham, D. Cruz, C. Reyes, B. J. Wiley, G. P. Lopez and B. B. Yellen, *Adv. Mater.*, 2015, **27**, 4725–4731.

14 B. Bharti, F. Kogler, C. K. Hall, S. H. Klapp and O. D. Velev, *Soft Matter*, 2016, **12**, 7747–7758.

15 D. B. Litt, M. R. Jones, M. Hentschel, Y. Wang, S. Yang, H. D. Ha, X. Zhang and A. P. Alivisatos, *Nano Lett.*, 2018, **18**, 859–864.

16 J. Ge and Y. Yin, *Angew. Chem. Int. Ed.*, 2011, **50**, 1492–1522.

17 H. S. Lee, T. S. Shim, H. Hwang, S. M. Yang and S. H. Kim, *Chem. Mater.*, 2013, **25**, 2684–2690.

18 J. B. Kim, S. Y. Lee, J. M. Lee and S. H. Kim, *ACS Appl. Mater. Interfaces*, 2019, **11**, 14485–14509.

19 V. A. Vasantha, W. Rusli, C. Junhui, Z. Wenguang, K. V. Sreekanth, R. Singh and A. Parthiban, *RSC Adv.*, 2019, **9**, 27199–27207.

20 J. B. Pendry, D. Schurig and D. R. Smith, *Science*, 2006, **312**, 1780–1782.

21 P. V. Braun and P. Wiltzius, *Nature*, 1999, **402**, 603–604.

22 J. D. Joannopoulos, P. R. Villeneuve and S. Fan, *Nature*, 1997, **386**, 143–149.

23 R. Elghanian, J. J. Storhoff, R. C. Mucic, R. L. Letsinger and C. A. Mirkin, *Science*, 1997, **277**, 1078–1081.

24 K. Saha, S. S. Agasti, C. Kim, X. Li and V. M. Rotello, *Chem. Rev.*, 2012, **112**, 2739–2779.

25 R. Karnik, F. Gu, P. Basto, C. Cannizzaro, L. Dean, W. Kyei-Manu, R. Langer and O. C. Farokhzad, *Nano Lett.*, 2008, **8**, 2906–2912.

26 S. Yadav, A. K. Sharma and P. Kumar, *Front. Bioeng. Biotechnol.*, 2020, **8**, 1–24.

27 W. Gao and J. Wang, *Nanoscale*, 2014, **6**, 10486–10494.

28 K. Rehman and M. H. Zulfakar, *Pharm. Res.*, 2017, **34**, 36–48.

29 I. F. Almeida, A. R. Fernandes, L. Fernandes, M. R. Pena Ferreira, P. C. Costa and M. F. Bahia, *Pharm. Dev. Technol.*, 2008, **13**, 487–494.

30 R. Parreira, E. Özelçi and M. S. Sakar, *Adv. Intell. Syst.*, 2020, **2**, 2000062.

31 S. Tsuchitani, T. Ikebe, H. Miki and K. Kikuchi, *Colloids Surf. A Physicochem. Eng. Asp.*, 2020.

32 X. Chen, C. Zhou, Y. Peng, Q. Wang and W. Wang, *ACS Appl. Mater. Interfaces*, 2020.

33 A. Leeth Holterhoff, V. Girgis and J. G. Gibbs, *ChemComm*, 2020.

34 W. F. Paxton, K. C. Kistler, C. C. Olmeda, A. Sen, S. K. St. Angelo, Y. Cao, T. E. Mallouk, P. E. Lammert and V. H. Crespi, *J. Am. Chem. Soc.*, 2004, **126**, 13424–13431.

35 W. F. Paxton, P. T. Baker, T. R. Kline, Y. Wang, T. E. Mallouk and A. Sen, *J. Am. Chem. Soc.*, 2006.

36 A. Kodama, Y. Sakuma, M. Imai, Y. Oya, T. Kawakatsu, N. Puff and M. I. Angelova, *Soft Matter*, 2016, **12**, 2877–2886.

37 M. Fialkowski, K. J. Bishop, R. Klajn, S. K. Smoukov, C. J. Campbell and B. A. Grzybowski, *J. Phys. Chem. B*, 2006, **110**, 2482–2496.

38 C. Wang, Q. Wang, R. F. Dong and Y. P. Cai, *Inorg. Chem. Commun.*, 2018, **91**, 8–15.

39 F. Soto, J. Wang, S. Deshmukh and U. Demirci, *Adv. Intell. Syst.*, 2021, **3**, 2000193.

40 B. A. Grzybowski, C. E. Wilmer, J. Kim, K. P. Browne and K. J. M. Bishop, *Soft Matter*, 2009, **5**, 1110–1128.

41 B. P. Isaacoff and K. A. Brown, *Nano Lett.*, 2017, **17**, 6508–6510.

42 M. Grzelczak, J. Vermant, E. M. Furst and L. M. Liz-Marzán, *ACS Nano*, 2010, **4**, 3591–3605.

43 S. O. Lumsdon, E. W. Kaler and O. D. Velev, *Langmuir*, 2004, **20**, 2108–2116.

44 J. J. Juárez and M. A. Bevan, *Adv. Funct. Mater.*, 2012, **22**, 3833–3839.

45 M. A. Grover, D. J. Griffin, X. Tang, Y. Kim and R. W. Rousseau, *J. Process Control*, 2020, **88**, 32–42.

46 H. Xie, M. Sun, X. Fan, Z. Lin, W. Chen, L. Wang, L. Dong and Q. He, *Sci. Robot.*, 2019, **4**, 1–14.

47 J. Palacci, S. Sacanna, A. P. Steinberg, D. J. Pine and P. M. Chaikin, *Science*, 2013, **339**, 936–940.

48 A. W. Long, J. Zhang, S. Granick and A. L. Ferguson, *Soft Matter*, 2015, **11**, 8141–8153.

49 D. J. Beltran-Villegas and M. A. Bevan, *Soft Matter*, 2011, **7**, 3280–3285.

50 X. Tang and M. A. Grover, *Annu. Rev. of Control Robot. Auton. Syst.*, 2022, **5**, 491–514.

51 L. Cademartiri and K. J. M. Bishop, *Nature materials*, 2015, **14**, 2–9.

52 K. John and M. Bär, *Physical review letters*, 2005, **95**, 198101.

53 A. Ashkin and L. Fellow, *IEEE J. Sel. Top. Quantum Electron.*, 2000, **6**, 841–856.

54 S. C. Chapin, V. Germain and E. R. Dufresne, *Opt. Express*, 2006, **14**, 13095.

55 J. A. Paulson, A. Mesbah, X. Zhu, M. C. Molaro and R. D. Braatz, *J. Process Control*, 2015, **27**, 38–49.

56 Y. Gao, B. W. Nyande and R. Lakerveld, *Comput. Chem. Eng.*, 2020, **139**, 106837.

57 A. Komaee and P. I. Barton, *IEEE Trans. Control Syst. Technol.*, 2017, **25**, 161–174.

58 D. Klotsa and R. L. Jack, *J. Chem. Phys.*, 2013, **138**, 094502.

59 T. Bäuerle, A. Fischer, T. Speck and C. Bechinger, *Nat. Commun.*, 2018, **9**, 1–8.

60 F. A. Lavergne, H. Wendehenne, T. Bäuerle and C. Bechinger, *Science*, 2019, **364**, 70–74.

61 C. L. Phillips and R. D. Harbor, *Feedback Control Systems*, Prentice Hall, 2000.

62 Y. Gao and R. Lakerveld, *AIChE J.*, 2019, **65**, 1–9.

63 Y. Gao and R. Lakerveld, *Lab Chip*, 2018, **18**, 2099–2110.

64 D. J. Griffin, X. Tang and M. A. Grover, *Proc. Am. Control Conf.*, 2016, **2016-July**, 3086–3091.

65 E. Camacho, C. Bordons and C. Alba, *Model Predictive Control*, Springer London, 2004.

66 Z. W. Ulissi, M. S. Strano and R. D. Braatz, *Comput. Chem. Eng.*, 2013, **51**, 149–156.

67 X. Tang, Y. Xue and M. A. Grover, *Proc. Am. Control Conf.*, 2013, 4228–4233.

68 X. Tang, B. Rupp, Y. Yang, T. D. Edwards, M. A. Grover and M. A. Bevan, *ACS Nano*, 2016, **10**, 6791–6798.

69 Y. Yang, R. Thyagarajan, D. M. Ford and M. A. Bevan, *J. Chem. Phys.*, 2016, **144**, 204904.

70 R. Lakerveld, G. Stephanopoulos and P. I. Barton, *J. Chem. Phys.*, 2012, **136**, 184109.

71 C. Gardiner, *Stochastic methods: a handbook for the natural and social sciences*, Berlin: Springer, 2009.

72 S. Ramaswamy, R. Lakerveld, P. I. Barton and G. Stephanopoulos, *Ind. Eng. Chem. Res.*, 2015, **54**, 4371–4384.

73 D. J. Griffin, M. A. Grover, Y. Kawajiri and R. W. Rousseau, *Ind. Eng. Chem. Res.*, 2016, **55**, 1361–1372.

74 M. Dijkstra and E. Luijten, *Nat. Mater.*, 2021, **20**, 762–773.

75 A. W. Long and A. L. Ferguson, *J. Phys. Chem. B*, 2014, **118**, 4228–4244.

76 M. Öner, F. C. Montes, T. Ståhlberg, S. M. Stocks, J. E. Bajtner and G. Sin, *Chem. Eng. Res. Des.*, 2020, **163**, 248–261.

77 A. Das and D. T. Limmer, *J. Chem. Phys.*, 2021, **154**, 014107.

78 A. L. Ferguson, *J. Phys.: Condens. Matter*, 2018, **30**, 043002.

79 J. H. Lee, *Int. Conf. Control Autom. Syst.*, 2011, 1807–1809.

80 Y. Xue, D. J. Beltran-Villegas, X. Tang, M. A. Bevan and M. A. Grover, *IEEE Trans. Control Syst. Technol.*, 2014, **22**, 1956–1963.

81 J. Zhang, J. Yang, Y. Zhang and M. A. Bevan, *Sci. Adv.*, 2020, **6**, 1–11.

82 S. Whitelam and I. Tamblyn, *Phys. Rev. E*, 2020, **101**, 1–13.

83 P. Kawak, D. S. Banks and D. R. Tree, *J. Chem. Phys.*, 2021, **155**, 214902.

84 R. R. Coifman and S. Lafon, *Appl. Comput. Harmon. Anal.*, 2006, **21**, 5–30.

85 J. O'Leary, R. Mao, E. J. Pretti, J. A. Paulson, J. Mittal and A. Mesbah, *Soft Matter*, 2021, **17**, 989–999.

86 A. W. Long, C. L. Phillips, E. Jankowksi and A. L. Ferguson, *Soft Matter*, 2016, **12**, 7119–7135.

87 W. F. Reinhart, A. W. Long, M. P. Howard, A. L. Ferguson and A. Z. Panagiotopoulos, *Soft Matter*, 2017, **13**, 4733–4745.

88 Z. M. Sherman, M. P. Howard, B. A. Lindquist, R. B. Jadrich and T. M. Truskett, *J. Chem. Phys.*, 2020, **152**, 140902.

89 W. D. Piñeros and T. Tlusty, *Phys. Rev. E*, 2021, **103**, 1–7.

90 B. A. Lindquist, *J. Chem. Phys.*, 2021, **154**, 174907.

91 M. R. Khadilkar, S. Paradiso, K. T. Delaney and G. H. Fredrickson, *Macromolecules*, 2017, **50**, 6702–6709.

92 C. L. Tsai and G. H. Fredrickson, *Macromolecules*, 2022.

93 S. Torquato, *Soft Matter*, 2009, **5**, 1157–1173.

94 A. Jain, J. A. Bollinger and T. M. Truskett, *AIChE J.*, 2014, **60**, 2732–2740.

95 M. Nguyen and S. Vaikuntanathan, *Proc. Natl. Acad. Sci. U.S.A. of the United States of America*, 2016, **113**, 14231–14236.

96 M. Nguyen, Y. Qiu and S. Vaikuntanathan, *Annu. Rev. of Condens. Matter Physics*, 2021, **12**, 273–290.

97 J. Ge, Y. Hu and Y. Yin, *Angew. Chem.*, 2007, **119**, 7572–7575.

98 Q. Fu, H. Zhu and J. Ge, *Adv. Funct. Mater.*, 2018, **28**,

1804628.
99 Z. Li, M. Wang, X. Zhang, D. Wang, W. Xu and Y. Yin, *Nano Lett.*, 2019, **19**, 6673–6680.
100 T. Tigges, T. Heuser, R. Tiwari and A. Walther, *Nano Lett.*, 2016, **16**, 7870–7874.
101 J. Byun, Y. Lee, J. Yoon, B. Lee, E. Oh, S. Chung, T. Lee, K. J. Cho, J. Kim and Y. Hong, *Sci. Robot.*, 2018, **3**, 1–12.
102 P. Taladriz-Blanco, N. J. Buurma, L. Rodríguez-Lorenzo, J. Pérez-Juste, L. M. Liz-Marzán and P. Hervés, *J. Mater. Chem.*, 2011, **21**, 16880–16887.
103 B. Su, J. P. Abid, D. J. Fermín, H. H. Girault, H. Hoffmannová, P. Krtil and Z. Samec, *J. Am. Chem. Soc.*, 2004, **126**, 915–919.
104 J. Han, M. C. Freyman, E. Feigenbaum and T. Yong-Jin Han, *ACS Photonics*, 2018, **5**, 1343–1350.
105 L. Lin, X. Peng, M. Wang, L. Scarabelli, Z. Mao, L. M. Liz-Marzán, M. F. Becker and Y. Zheng, *ACS Nano*, 2016, **10**, 9659–9668.
106 A. Yethiraj, J. H. Thijssen, A. Wouterse and A. Van Bladderen, *Adv. Mater.*, 2004, **16**, 596–600.
107 B. Liu, T. H. Besseling, M. Hermes, A. F. Demirörs, A. Imhof and A. Van Blaaderen, *Nat. Commun.*, 2014, **5**, 1–8.
108 J. J. Crassous, A. M. Mihut, E. Wernersson, P. Pfleiderer, J. Vermant, P. Linse and P. Schurtenberger, *Nat. Commun.*, 2014, **5**, 1–7.
109 S. Samai, Z. Qian, J. Ling, K. N. Guye and D. S. Ginger, *ACS Applied Materials and Interfaces*, 2018, **10**, 8976–8984.
110 L. Moscardi, G. Lanzani, G. M. Paternò and F. Scotognella, *Appl. Sci.*, 2021, **11**, 2119.
111 C. Ropp, Z. Cummins, S. Nah, S. Qin, J. H. Seog, S. B. Lee, J. T. Fourkas, B. Shapiro and E. Waks, *Nano Letters*, 2013, **13**, 3936–3941.
112 E. O. P. Solis, P. I. Barton and G. Stephanopoulos, *Ind. Eng. Chem. Res.*, 2010, **49**, 7728–7745.
113 E. O. P. Solis, P. I. Barton and G. Stephanopoulos, *Ind. Eng. Chem. Res.*, 2010, **49**, 7746–7757.
114 K. A. Komarov and S. O. Yurchenko, *J. Chem. Phys.*, 2021, **155**, 114107.
115 S. Shabaniverki and J. J. Juárez, *Micromachines*, 2021, **12**, 935.
116 A. Hensley, W. M. Jacobs and W. Benjamin Rogers, *Proceedings of the National Academy of Sciences of the United States of America*, 2022, **119**, e2114050118.
117 J. F. Shackelford, *Introduction to Materials Science for Engineers*, New York: Macmillan, 2005.
118 X. Yu and Y. Han, in *Directed Self-assembly of Block Copolymers for Nano-manufacturing*, ed. R. Gronheid and P. Nealey, Woodhead Publishing, 2015, pp. 47–66.
119 J. W. Swan, J. L. Bauer, Y. Liu and E. M. Furst, *Soft Matter*, 2014, **10**, 1102–1109.
120 P. K. Kao, B. J. VanSaders, S. C. Glotzer and M. J. Solomon, *Sci. Rep.*, 2021, **11**, 1–13.
121 Z. M. Sherman and J. W. Swan, *ACS Nano*, 2016, **10**, 5260–5271.
122 Z. M. Sherman and J. W. Swan, *ACS Nano*, 2019, **13**, 764–771.
123 H. Kim, M. Sau and E. M. Furst, *Langmuir*, 2020, **36**, 9926–9934.
124 A. Sorrenti, J. Leira-Iglesias, A. J. Markvoort, T. F. De Greef and T. M. Hermans, *Chem. Soc. Rev.*, 2017, **46**, 5476–5490.
125 Y. Yan, J. Huang and B. Z. Tang, *ChemComm*, 2016, **52**, 11870–11884.
126 L. Di Michele, F. Varrato, J. Kotar, S. H. Nathan, G. Foffi and E. Eiser, *Nat. Commun.*, 2013, **4**, 1–7.
127 K. A. Dawson, *Curr. Opin. Colloid Interface Sci.*, 2002, **7**, 218–227.
128 F. Sciortino and P. Tartaglia, *Adv. Phys.*, 2005, **54**, 471–524.
129 L. C. Cheng, P. D. Godfrin, J. W. Swan and P. S. Doyle, *Soft Matter*, 2018, **14**, 5604–5614.
130 L. C. Cheng, S. L. Kuei Vehusheia and P. S. Doyle, *Langmuir*, 2020, **36**, 3346–3355.
131 J. N. Immink, J. J. Maris, J. J. Crassous, J. Stenhammar and P. Schurtenberger, *ACS Nano*, 2019, **13**, 3292–3300.
132 K. T. Wu, L. Feng, R. Sha, R. Dreyfus, A. Y. Grosberg, N. C. Seeman and P. M. Chaikin, *Proc. Natl. Acad. Sci. U.S.A. of the United States of America*, 2012, **109**, 18731–18736.
133 M. Numata, *Chem. Asian J.*, 2015, **10**, 2574–2588.
134 X. S. Miao, L. P. Shi, P. K. Tan, J. M. Li, K. G. Lim, X. Hu and T. C. Chong, *Appl. Opt.*, 2004, **43**, 1140.
135 A. Nemati, Q. Wang, M. H. Hong and J. H. Teng, *Optoelectron. Adv.*, 2018, **1**, 1–25.
136 K. Stratford, O. Henrich, J. S. Lintuvuori, M. E. Cates and D. Marenduzzo, *Nat. Commun.*, 2014, **5**, 1–8.
137 C. L. Phillips, E. Jankowski, B. J. Krishnatreya, K. V. Edmond, S. Sacanna, D. G. Grier, D. J. Pine and S. C. Glotzer, *Soft Matter*, 2014, **10**, 7468–7479.
138 S. Mann, *Nature Materials*, 2009, **8**, 781–792.
139 S. Whitelam and R. L. Jack, *Annual Review of Physical Chemistry*, 2015, **66**, 143–163.
140 R. K. Grötsch, C. Wanzke, M. Speckbacher, A. Angı, B. Rieger and J. Boekhoven, *J. Am. Chem. Soc.*, 2019, **141**, 9872–9878.
141 J. Yan, M. Han, J. Zhang, C. Xu, E. Luijten and S. Granick, *Nat. Mater.*, 2016, **15**, 1095–1099.
142 F. Soto, E. Karshalev, F. Zhang, B. Esteban Fernandez de Avila, A. Nourhani and J. Wang, *Chem. Rev.*, 2022, **122**, 5365–5403.
143 J. Yan, M. Bloom, S. C. Bae, E. Luijten and S. Granick, *Nature*, 2012, **491**, 578–581.
144 S. Ilday, G. Makey, G. B. Akguc, Ö. Yavuz, O. Tokel, I. Pavlov, O. Gülseren and F. Ömer Ilday, *Nat. Commun.*, 2017, **8**, 14942.
145 B. Zhang, A. Snezhko and A. Sokolov, *Phys. Rev. Lett.*, 2022, **128**, 018004.
146 D. P. Singh, U. Choudhury, P. Fischer and A. G. Mark, *Adv. Mater.*, 2017, **29**, 1–7.
147 M. M. Norton, P. Grover, M. F. Hagan and S. Fraden, *Phys.*

Rev. Lett., 2020, **125**, 178005.

148 W. Peng, S. Zhu, W. Zhang, Q. Yang, D. Zhang and Z. Chen, *Nanoscale*, 2014, **6**, 6133–6140.

149 Q. Li, Q. Zeng, L. Shi, X. Zhang and K. Q. Zhang, *J. Mater. Chem. C*, 2016, **4**, 1752–1763.

150 V. Saranathan, C. O. Osuji, S. G. Mochrie, H. Noh, S. Narayanan, A. Sandy, E. R. Dufresne and R. O. Prum, *Proc. Natl. Acad. Sci. U.S.A. of the United States of America*, 2010, **107**, 11676–11681.

151 J. Teyssier, S. V. Saenko, D. Van Der Marel and M. C. Milinkovitch, *Nat. Commun.*, 2015, **6**, 1–7.

152 F. Ling, Z. Zhong, R. Huang and B. Zhang, *Sci. Rep.*, 2018, **8**, 1–9.

153 J. A. Fan, C. Wu, K. Bao, J. Bao, R. Bardhan, N. J. Halas, V. N. Manoharan, P. Nordlander, G. Shvets and F. Capasso, *Science*, 2010, **328**, 1135–1138.

154 S. Zhang, Y.-S. Park, J. Li, X. Lu, W. Zhang and X. Zhang, *Phys. Rev. Lett.*, 2009, **102**, 023901.

155 E. Plum, J. Zhou, J. Dong, V. A. Fedotov, T. Koschny, C. M. Soukoulis and N. I. Zheludev, *Phys. Rev. B*, 2009, **79**, 035407.

156 T. Lv, Y. Li, H. Ma, Z. Zhu, Z. Li, C. Guan, J. Shi, H. Zhang and T. Cui, *Sci. Rep.*, 2016, **6**, 1–9.

157 M. Liu, E. Plum, H. Li, S. Li, Q. Xu, X. Zhang, C. Zhang, C. Zou, B. Jin, J. Han and W. Zhang, *Adv. Funct. Mater.*, 2021, **31**, 2010249.

158 S. Adepu and S. Ramakrishna, *Molecules*, 2021, **26**, 5905.

159 S. Singh and J. Moran, *Micromachines*, 2021, **12**, 1216.

160 J. L. Anderson and D. C. Prieve, *Sep. Purif. Methods*, 1984, **13**, 67–103.

161 B. Sabass and U. Seifert, *J. Chem. Phys.*, 2012, **136**, 064508.

162 M. Lisicki, S. Y. Reigh and E. Lauga, *Soft Matter*, 2018, **14**, 3304–3314.

163 A. Subrizi, E. M. Del Amo, V. Korzhikov-Vlakh, T. Tennikova, M. Ruponen and A. Urtti, *Drug discovery today*, 2019, **24**, 1446–1457.

164 H. Al-Obaidi and A. T. Florence, *Journal of Drug Delivery Science and Technology*, 2015, **30**, 266–277.

165 S. Vinogradov, *Curr. Pharm. Des.*, 2006, **12**, 4703–4712.

166 R. D. Field, P. N. Anandakumaran and S. K. Sia, *Appl. Phys. Rev.*, 2019, **6**, 041305.

167 S. Fusco, M. S. Sakar, S. Kennedy, C. Peters, R. Bottani, F. Starsich, A. Mao, G. A. Sotiriou, S. Pané, S. E. Pratsinis *et al.*, *Adv. Mater.*, 2014, **26**, 952–957.

168 H. Hezaveh and I. I. Muhamad, *Chem. Eng. Res. Des.*, 2013, **91**, 508–519.

169 N. Rasool, T. Yasin, J. Y. Heng and Z. Akhter, *Polymer*, 2010, **51**, 1687–1693.

170 W. G. Pitt, G. A. Husseini and B. J. Staples, *Expert Opin. Drug Deliv.*, 2004, **1**, 37–56.

171 N. M. Salkho, V. Paul, P. Kawak, R. F. Vitor, A. M. Martins, M. Al Sayah and G. A. Husseini, *Artif. Cells Nanomed. Biotechnol.*, 2018, **46**, 462–472.

172 C. Kaspar, B. J. Ravoo, W. G. van der Wiel, S. V. Wegner and W. H. Pernice, *Nature*, 2021, **594**, 345–355.

173 F. Fu, Z. Chen, Z. Zhao, H. Wang, L. Shang, Z. Gu and Y. Zhao, *Proc. Natl. Acad. Sci. U.S.A. of the United States of America*, 2017, **114**, 5900–5905.

174 H. Zhang, X. Bu, S. Yip, X. Liang and J. C. Ho, *Adv. Intell. Syst.*, 2020, **2**, 1900085.

175 X. Zhang, L. Chen, K. H. Lim, S. Gonuguntla, K. W. Lim, D. Pranantyo, W. P. Yong, W. J. T. Yam, Z. Low, W. J. Teo, H. P. Nien, Q. W. Loh and S. Soh, *Adv. Mater.*, 2019, **31**, 1804540.

176 J. M. Parrilla-Gutierrez, A. Sharma, S. Tsuda, G. J. Cooper, G. Aragon-Camarasa, K. Donkers and L. Cronin, *Nature communications*, 2020, **11**, 1–8.

177 S. Y. Guo, P. Friederich, Y. Cao, T. C. Wu, C. J. Forman, D. Mendoza, M. Degroote, A. Cavell, V. Krasecki, R. J. Hickman *et al.*, *Matter*, 2021, **4**, 1107–1124.

178 A. C. Cavell, V. K. Krasecki, G. Li, A. Sharma, H. Sun, M. P. Thompson, C. J. Forman, S. Y. Guo, R. J. Hickman, K. A. Parrish *et al.*, *Chemical science*, 2020, **11**, 2647–2656.

179 Y. Fang, V. V. Yashin, S. P. Levitan and A. C. Balazs, *Chemical Communications*, 2017, **53**, 7692–7706.

180 S. R. White, J. S. Moore, N. R. Sottos, B. P. Krull, W. A. S. Cruz and R. C. R. Gergely, *Science*, 2014, **344**, 620–623.

181 F. Zhang, P. Ju, M. Pan, D. Zhang, Y. Huang, G. Li and X. Li, *Corros. Sci.*, 2018, **144**, 74–88.

182 C. Liang, J. Li, M. Xia, G. Li and Y. Luo, *Polymers*, 2017, **9**, 200.

183 Z. Hu, D. Zhang, F. Lu, W. Yuan, X. Xu, Q. Zhang, H. Liu, Q. Shao, Z. Guo and Y. Huang, *Macromolecules*, 2018, **51**, 5294–5303.

184 X. Dong, S. Gao, J. Huang, S. Li, T. Zhu, Y. Cheng, Y. Zhao, Z. Chen and Y. Lai, *J. Mater. Chem. A*, 2019, **7**, 2122–2128.

185 E. Ahmed, D. P. Karothu, M. Warren and P. Naumov, *Nature Communications*, 2019, **10**, 3723.

186 S. Kobatake, S. Takami, H. Muto, T. Ishikawa and M. Irie, *Nature*, 2007, **446**, 778–781.

187 S.-N. Yin, J. Liu, D. Wu, S. Chen and W. Xia, *ACS Applied Polymer Materials*, 2020, **2**, 448–454.

188 H. Massana-Cid, F. Meng, D. Matsunaga, R. Golestanian and P. Tierno, *Nature Communications*, 2019, **10**, 2444.

189 Y. Ma, P. He, W. Xie, Q. Zhang, W. Yin, J. Pan, M. Wang, X. Zhao and G. Pan, *Research*, 2021, **2021**, 1–11.

190 S. Lee, H. A. Calcaterra, S. Lee, W. Hadibrata, B. Lee, E. Oh, K. Aydin, S. C. Glotzer and C. A. Mirkin, *Nature*, 2022.

191 F. Nan and Z. Yan, *Angewandte Chemie International Edition*, 2019, **58**, 4917–4922.

192 J. Liu, P. Ming and S. Li, *Int. J. Control Autom. Syst.*, 2016, **14**, 1223–1230.

193 L. Ma, Z. Wang, Q. L. Han and Y. Liu, *Sci. China Inf. Sci.*, 2017, **60**, 1–15.

194 R. Olfati-Saber, *IEEE Trans. Automat. Contr.*, 2006, **51**, 401–420.

195 C. L. Tsai, K. T. Delaney and G. H. Fredrickson, *Macromolecules*, 2016, **49**, 6558–6567.