Digital Colloids: Reconfigurable Clusters as High Information Density Elements

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Through the design and manipulation of discrete, nanoscale systems capable of encoding massive amounts of information, the basic components of computation are open to reinvention. These components enable tagging, memory storage, and sensing in unusual environments – elementary functions crucial for soft robotics and “wet computing”. Here we show how reconfigurable clusters made of $N$ colloidal particles bound flexibly to a central colloidal sphere have the capacity to store an amount of information that increases as $O(N!)$. Using Brownian dynamics simulations, we predict dynamical regimes that allow for information to be written, saved, and erased. We experimentally assemble an $N = 4$ reconfigurable cluster from chemically
synthesized colloidal building blocks, and monitor its equilibrium dynamics. We observe state switching in agreement with simulations. This cluster can store one bit of information, and represents the simplest digital colloid.

The physical limitations to increasing transistor density on silicon-based computing platforms demand we consider alternative ways to store and manipulate data. New technologies such as autonomous “softbots” [1] and 3D printing of high-functioning materials [2,3,4] are driving the need for novel approaches to fast-switching memory elements, high information density storage, and massively parallel computation. As we work towards Avogadro-scale computers we must identify new analogues to the logic gates underlying circuit-based architectures [5]. Computing architectures based on the dynamics of thermodynamically large ensembles of microscopic colloidal particles can take advantage of stochastic parallelism to perform astronomical numbers of calculations simultaneously [6]. Such colloidal computational elements could be dispersed throughout a medium to perform in situ calculations based on the locally available data, or to store information in an easily transported fluid medium.

Massively parallel and dispersed computation and storage require thinking outside of traditional integrated circuit computing paradigms where bits and bytes are wed to silicon components. Alternative approaches to traditional computation include computing with DNA [7,8,9,10], Belousov-Zhabotinsky chemical reactions [11], microfluidic bubble circuits [12] and chemosensors [13]. Of these alternative approaches to computation, DNA computing has received the most attention and has advanced the furthest. The storage capabilities of DNA were recently highlighted with the writing and subsequent reading of a 5.25-megabit book on DNA [14].

The objective of using new digital nanostructures should not be to simply emulate digital processes in silica. Alternative computing paradigms designed for massively parallel and distributed systems include amorphous computing [15]: a new branch of computational science that studies how coherent functional behavior can be achieved from distributed, asynchronous, locally interacting, computing elements. Servat and Drogoul [16] propose that a new powerful form of computing could be realized by constructing an amorphous
computing medium from a population of light-weight computing elements that respond to changes in their environment through self-organization. We propose that a system of reconfigurable colloidal particles is a natural candidate for such a system.

Recent advances in colloidal synthesis [17,18] have created a vast design space of particles with precisely engineered sizes and shapes whose interactions with other particles are both directional and specific. Dispersions of such colloidal particles constitute new paradigms of programmable matter [19]. Two recent examples of particular relevance to the present work are dimpled colloidal spheres with shape-specific interactions [20,21] which can be assembled into reconfigurable clusters. Information stored in colloidal materials can be retrieved in a variety of ways, from direct observation via optical microscopy to inference based on macroscopic properties. Here, we describe how these features may be combined to create high-density computing elements that we dub digital colloids.

Digital colloids are defined by three essential characteristics. First, each cluster must be able to switch among distinguishable microstates, referred to below as simply “states”, each with equal probability of occurrence. The set of all such states determines the amount of information that a cluster can store. A cluster with two unique states, for example, can store one bit, while a cluster with 256 unique states can store a byte. Second, it must be possible to disable or enable the clusters’ ability to switch. Locking a cluster’s configuration preserves its information for readout. Unlocking enables the cluster to perform computations. Third, a method must be available to set a cluster’s state deterministically under external control, thereby allowing information to be stored and algorithms to be programmed. After describing a class of colloidal clusters that have the properties of digital colloids, we present a working experimental realization of a two-state, switchable, digital colloidal element capable of storing a single bit of information. We conclude by proposing several examples of how digital colloids can be used in practical applications. Just as Ref [7] changed the way we think about performing computation by introducing the idea of “soft computation”, we anticipate that reconfigurable colloidal clusters like those we propose here may be used as distributed information storage devices in environments that break free from the limitations of silicon-based computing, permitting novel ways to perform
sensing and computing in solvent-based chemical processes and biological systems, and may even provide ways to interface traditional computers with computations being performed in the bloodstream or brain.

Figure 1. (Color) Left image: an $N = 6$, octahedral cluster. The outer spheres are transparent so the central particle can be seen. Middle image: the $N = 6$ cluster labeled with six colors. On the right, a table shows the point group, rotational symmetry, and the maximum number of storable states for each $N$-cluster.

Our design for digital colloids is motivated by the *spherical code* problem. A long-studied mathematical problem, the $N$th spherical code (SC) solution [22,23,24] gives the densest packing of $N$ hard spheres of diameter $d$ around a central sphere of unit diameter. The densest packing for any $N$ is achieved for a diameter ratio $\Lambda_{SC} = 1/d_{SC}$. Values of $\Lambda_{SC}$ are tabulated for up to $N = 130$ in reference [25]. A cluster of $N$ spheres in its spherical code structure (Fig. 1) can store information related to the number of distinguishable configurations. The number of distinguishable configurations for a cluster of $N$ distinguishable spheres is $N!/\sigma$, where $\sigma$ is the rotational symmetry of the cluster. In Fig. 1, an example $N = 6$ cluster, which has an octahedral structure, is shown with six distinguishable outer spheres. The table in Fig. 1 provides the rotational symmetry and the maximum number of unique states for each spherical code structure up to $N = 12$. The $N = 4$ cluster has two states that are mirror symmetries; this colloidal element can thus store a single bit. As $N$ increases, clusters have an increasing number of distinguishable structures. A colloidal structure of 11 or 12 distinguishable spheres can store over 30 KB of information in its spherical code structure.
Figure 2. (Color) Left to right: The spherical code structure, Λ_{SC}, unique rearrangement, transition structure, and Λ_T for each cluster. The outer spheres in each rearrangement are colored so that the change in the cluster can be observed. The bonds (black) in the structures indicate spheres in contact.

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In addition to the ability to store information, a digital colloid used for memory or computing must be able to switch – when appropriate – among the various distinguishable states accessible to it. The dynamics exhibited by an $N$-cluster can be described in terms of three distinct regimes of $\Lambda$: forbidden, locked, and unlocked (See SI-I). If $\Lambda < \Lambda_{SC}$, the cluster is geometrically forbidden. If $\Lambda_{SC} < \Lambda < \Lambda_T$, the outer spheres are below their densest packing limit, and each sphere is caged by its neighbors and restricted to rattling about its spherical code coordinates. In this range each cluster remains locked in an identifiable state given by its spherical code structure. If $\Lambda > \Lambda_T$ the spheres are no longer caged and can rearrange to sample all of the states available to the cluster. $\Lambda_T$ is thus the diameter ratio above which the outer spheres may permute so that transitions ($T$) among states may occur. We refer to a cluster in the regime $\Lambda > \Lambda_T$ as “unlocked”. Fig. 2 shows the spherical code structure, point group symmetry, name of the convex polyhedron formed by the cluster (for those with names), and values of $\Lambda_{SC}$ and $\Lambda_T$ for each cluster in the range $N = 4 - 12$.

![Graph and images]

Figure 3. (a) For $N = 4$, simulations predict state switching becomes measurable and increases rapidly for $\Lambda > \Lambda_T$. (b) An SEM micrograph of lock-and-key colloidal particles used to create the tetrahedral $N = 4$ cluster shown in (c). (d) The cluster in its planar transition state. (e) A time series of micrographs showing typical reconfigurations of the cluster. Red bars indicate the planar transition state and green bars indicate tetrahedral order. Movies of the cluster dynamics and switching mechanism are in the SI.
When $\Lambda \geq \Lambda_T$, the outer spheres can undergo a finite set of cooperative rearrangements, limited by crowding on the surface of the central sphere. When $\Lambda >> \Lambda_T$, there is sufficient excess surface area that the dynamics of the outer spheres are uncorrelated. The rearrangement pathways when $\Lambda \geq \Lambda_T$ are unique to $N$ and are reminiscent of the twisting of a Rubik’s Cube™, the popular three-dimensional puzzle. Because each rearrangement follows a transition path between two identical spherical code structures, there is a midpoint on the path where the structure of the cluster is halfway between the two states. This transition state, which has mirror symmetry, is a saddle-point structure that the cluster must be able to form in order to rearrange. This transition state structure can be geometrically constructed, and the precise value of $\Lambda_T$ for any $N$ may be numerically derived as the smallest $\Lambda$ for which the spheres can fit in the required shape (details in SI-II). One exception to the transition pathway description is the $N = 5$ cluster [26], for which there is a continuum of structures, rather than a single, unique, transition structure (SI-III). The other exception is the $N = 12$ cluster, which has two (possibly non-distinct) modes for rearranging its structure at $\Lambda_T$ (SI-IV and SI-Movies).

An illustration of the cluster rearrangements and transition structures for every $N$ is presented in Fig. 2. For the spherical code and transition structures, the black bonds represent spheres in contact. Although each cluster has a distinct transition path, the rotational symmetry of the cluster and chiral symmetry of the permutations imply there are multiple symmetrically equivalent ways the rearrangement can be excited in a given cluster. For example, there are five ways an $N = 11$ cluster can rearrange. As shown in Figure 3 (and SI-I), the rate of switching between states is sensitive to $\Lambda$. Movies of the rearrangements and a more detailed description of each can be found in SI-IV.

The predicted internal rearrangements of these digital clusters have two important consequences for information storage. First, every possible state can be reached by a sequence of rearrangements when $\Lambda > \Lambda_T$. This is demonstrated by showing that the group product of the rearrangement group and rotational symmetry group is equal to the symmetric group; details in SI-V. Second, rearrangements can be switched on or off by toggling $\Lambda$ about $\Lambda_T$. Consequently, a cluster’s state may be erased by unlocking the cluster.
(Λ > Λ_T), and a new state may be stored by locking it again (Λ < Λ_T) after the cluster has rearranged.

The smallest cluster with at least two distinct states is the N = 4 cluster. Our simulations predict the 4-cluster has tetrahedral symmetry, and so is capable of storing two states of opposite mirror symmetry when all four outer spheres are distinguishable from each other. We target a prototype tetramer for experimental realization. In Figure 3 we show an example of a 4-cluster assembled from 1.8µm-diameter colloidal particles dispersed in a density matched fluid medium. The particles are synthesized from monodisperse oil droplets via a free-radical polymerization. Each outer particle has a dimple formed by controlled buckling of the droplet’s polymerized shell [21] whose curvature matches that of the central sphere. Four such dimpled particles can mate to each sphere, and are held in place by a depletion interaction [20] that yields thermodynamically stable clusters while still allowing the outer particles to move freely across the inner sphere’s surface. Large quantities of these reconfigurable colloidal clusters self-assemble in highly concentrated suspensions. They are most easily visualized and analyzed, however, at low concentrations. The clusters used in this study therefore were assembled manually using holographic optical tweezers [27,28]. Considerable effort was expended to ensure that the assembled clusters are neutrally buoyant so their behavior can be observed over periods extending to half an hour or more. Digital video images of the freely diffusing clusters were analyzed using specialized software [29] to track each of the particles in each of the clusters individually.

Accounting for the dimple, the cluster in Fig. 3 has Λ ≈ 0.61. Based on our predicted value of Λ_T = 0.4142 (Fig. 2), this cluster should be unlocked and free to switch between states. To test this, we monitor the motion of the outer particles by recording their positions at a sufficiently high frame rate and tracking their relative positions within the cluster. We observe that the cluster is usually found in a tetrahedral structure like that shown in Fig. 3c. From time to time, however, it switches from one tetrahedral configuration to the equivalent structure with mirror symmetry. Further, we observe that this rearrangement occurs via the predicted planar transition structure (Fig. 3d), confirming the transition
pathway anticipated in Fig. 2. To our knowledge, this is the first realization of a digital colloidal cluster. A description of the experimental procedure can be found in SI-VI and short movies of the cluster dynamics and state switching can be found in the online supplemental materials.

The 4-cluster is the largest reconfigurable spherical code cluster we attempted to make. Although larger $N$-clusters can be assembled using holographic optical tweezers, the serial nature of this technique precludes scaling to the large numbers of clusters desired for practical applications. Self-assembly offers an attractive alternative way to assemble large numbers of digital colloids of higher complexity. Simulations suggest that stable $N$-clusters will self-assemble from a bath of spheres if the outer spheres stick only to the inner spheres and if the diameter ratio $\Lambda$ of outer to inner spheres exceeds $\Lambda_{SC}$ [26]. Recent advances in colloidal synthesis and assembly suggest this should soon be possible. One particularly exciting route is the recent use of self-assembled colloidal crystals to template the fabrication of $N=12$ clusters, bringing the realization of 30 KB digital colloids within reach [30]. At just 3% concentration, a thimble-full of digital colloids in solution could store as much as a petabyte of information.

In practice, digital colloids can store only as much information as can be written onto them and reliably read out. Fluorescent labeling could be used to create information-rich switchable clusters with distinguishable configurations. Locking and unlocking may be achieved by functionalizing the central sphere to swell or shrink in response to applied electric fields, changes in temperature, or changes in solvent composition [31,32]. Research efforts along these lines are underway.

Beyond the use of imaging, writing and reading states may be achievable in other ways. Perhaps the simplest example is checking whether two specific labeled spheres are in contact with each other. If an attractive or repulsive force can be induced between two spheres in the unlocked cluster (for $N > 4$, Fig. 4a), then the cluster will rearrange to adopt a state where the two spheres are or are not in contact, respectively. Such forces could be mediated by polymer brushes bound to the spheres’ surfaces, a screened electrostatic potential, or the introduction of an amphiphile that binds to a specific sphere pair when
they are in close proximity. The particle’s state then could be read out with chemical reporters or by exploiting changes in optical properties associated with changes in structure [33]. If it is possible to determine whether any two spheres are neighbors, then the state of a cluster can be determined to within a mirror symmetry operation, or half of the theoretical maximum of the table in Fig. 2.

The ability of reconfigurable colloidal clusters to store states and the sensitive control of the rate of switching between states suggests that such digital clusters may have a rich potential set of applications as small, information-storage elements. For example, a population of locked, identical $N$-clusters could be mixed into a controlled substance as a colloidal “bar code” that uniquely identifies the material’s origin. Digital colloids also could constitute a new class of sensors, devices capable of changing state in the presence of an external agent. Reconfigurable colloidal components could be designed to self-assemble into different mesoscale structures with measurable properties dependent on the clusters’ state. For example, a locked $N = 12$ cluster, composed of two types of outer spheres randomly labeled, is shown in Fig. 4(b). The interaction between the two types is designed to drive the spheres to de-mix when unlocked. When exposed to an environmental stimulus that unlocks the clusters, e.g. one that swells the central particle, our simulations predict the two outer sphere types separate and the cluster becomes a Janus particle [34].

Another class of sensors could be created from a population of 4-clusters that are locked into a specific state and are designed to unlock when exposed to a certain environmental stimulus. When redispersed, an unlocked population of clusters would relax to a statistically uniform state that would signal the influence of the target stimulus. The difference could be observed macroscopically through the self-organization of the clusters, as illustrated in Fig. 4c (SI-VII).

Digital colloids also could act as a platform for localizing and controlling the transport of DNA-encoded information. Specific labels, for example, could be realized by grafting short oligonucleotides to the outer spheres prior to assembly [35,36,37]. Such hybrid DNA/nanoparticle components have already demonstrated potential in creating controllable assemblies. Although we describe here just a few envisioned uses of digital
colloids, with targeted effort they could inspire a range of new nanoscale technologies with real-world applications.

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Figure 4. (Color) (a) Schematic showing a cluster with two states determined by whether or not the red and green spheres are neighbors. Polymer brushes, block copolymers than bind to the spheres, and interactions with light may enable the states to be controlled and measured. (b) An $N = 12$ cluster with two immiscible particle types reconfigures to a Janus cluster when it is exposed to a target chemical, swelling the central particle so as to unlock the cluster. (c) Two populations of 4-clusters are combined to self-assemble. Simulations predict two different resulting assemblies depending on whether the clusters have the same or opposite chirality.
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