Assembly of nanocube super-structures
directed by surface and magnetic interactions

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Abstract

We model the stabilization of clusters and lattices of cuboidal particles with long-ranged magnetic dipolar and short-ranged surface interactions. Two realistic systems were considered: one with magnetization orientated in the [001] crystallographic direction, and the other with magnetization along the [111] direction. We have studied magnetic nanocubes clusters in the limit of $T = 0$ K, intending to elucidate the structural genesis of low energy configurations. Our results demonstrate that dipolar coupling can stabilize nanoparticle assemblies with cubic, planar, and linear arrangements seen previously in experiments. While attractive surface energy supports the formation of super-cubes, the repulsion results in the elongated structures in the form of rods and chains. We observe the stabilization of the ferromagnetic planar arrangements of the cubes standing on their corners and in contact over edges. We illustrate that minimal energy structures depend only on the size of the assembly and balance of surface repulsion and magnetic dipolar coupling. The presented results are scalable to different particle sizes and material parameters.
Introduction

Assembly of nanoparticles into target functional structures refers to the spontaneous formation of ordered patterns from disordered constituents. The self and directed assembly of magnetic particles carrying permanent dipolar moment is of great interest for many technical applications. In some cases, complex superstructures are created in the sequence of steps in which first particles are formed, and the interactions between nanoparticles are carefully tuned to steer whole self-assembly process to ultimately form macroscale ordered structure. Applications rely on outstanding assembly properties of magnetic nanoparticles, and therefore, the understanding of relevant energetic scales is crucial for designing processes including magnetorheological fluids, high-density magnetic storage devices, and tailored superlattices. The magnetic spheres and corresponding dipolar hard-sphere model, with a point-dipole at the center of a spherically symmetric hardcore, is one the most studied systems both in the experiment and theoretically due to the simplicity of representation for particles with magnetic interactions.

In contrast, cuboid particle geometry has received less attention despite advantageous for many applications in terms of photonic response, improved catalytic activity, packing density, and orientability. Still, the cubic shape is unique in two ways. First, this shape imposes strong coupling between geometry and magnetic interaction in assemblies of magnetic particles, where interparticle junctions formed by cube over their surfaces, corners, and edges are stabilized by strong attractive magnetic forces. Second, it is a compelling geometry for obtaining non-close-packed assemblies by designing surface interaction through facets. The magnetic forces are not screened in solution and are virtually independent of changes in experimental conditions such as humidity, pH, or solvent composition, which can alter surface interactions, thus, giving us significant design freedom. It is worth noting that particles with significant shape anisotropy can remain single domain at much larger sizes than their spherical counterparts. From a fundamental point of view, by looking into the self-assembled structure we can in-revers conclude about interactions present in the system. There is an important reason to investigate monodispersed mag-

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1 Assemblies where particles have an average number of face-to-face touching neighbors less than five.
Figure 1: SEM images of polymorphs composed of (A) silica coated and (B) bare hematite microcuboids. Adapted with permission from ref. [15] and ref. [14] respectively. (C) Optical microscopy images of hematite cuboids during particle self-assembly induced by sedimentation. Adapted with permission from ref. [19] (D) Self-assembled chain in gas phase of 25 nm iron/iron-oxide core/shell magnetic nanocubes, adapted with permission from ref. [17] (E) SEM image of a 3D cuboid which consists of more than 10,000 iron-oxide nanocubes. Adapted with permission from ref. [13] (F) Top and (G) side-view SEM images of self-assembled one-dimensional nanocube ribbons, adapted with permission from ref. [6] (H) Magnified TEM images of 2D lattice nickel nanocube lattice (cubes are suspended on corners) and (J) STEM image of Ni nanocubes. Adapted with permission from ref. [20]

Magnetic cubes: atomically flat sides of nanocubes allow them to glide almost without friction over their superstructures. [17] Besides, square symmetry reduces the number of local energetic minima in which the system can be quenched, preventing the creation of the clumps, [13] while tailoring the magnetic properties of the nanoparticles can provide an effective approach to direct self-assembly process. [14, 18] Here, we analyze magnetic nanocubes in which interaction landscape is defined by the steric effect, and magnetic and surface interactions. [12, 17, 19]

Figure 1 summarises the magnetic nanocuboid structure stabilized by an interplay of density, magnetic anisotropy, the strength of dipolar coupling, and surface interactions. If the density of particles is low, small clusters might be created. [13] The hematite micron-sized cuboids demonstrate how dipolar interactions and particle shape result in the creation of the regular polymorphs, cf., Figure 1A–C. Designing a rational assembly mechanism based on magnetostatic interactions requires understanding differences between the energies of different structures. Strong and long-ranged dipolar coupling leads to the formation of macroscopic chains even in the gas phase, from particles coming from the cluster source, as demonstrated in Figure 1D from Ref. [12] The colloidal cubic particles assembled into 3D structures with remarkable internal order, e.g., regular super-
cubes composed of up to 10000 nanocubes in Figure 1E from Ref. 13. In the presence of a parallel external magnetic field, Singh et al. 6 observed the formation of three nanocube wide stripes at low densities and super-rods composed of arrays of nanocubes tilted 45° relative to rod axis (see Figure 1F,G). Chemistry of solution in which particles are created, i.e., presence of chloride ions and fatty acids, which control growth and prevent agglomeration result also in strong repulsion of the particles. Figure 1J adapted for Ref., 20 shows two-dimensional crystal formed by cubic-shaped particles standing on their corners, which is the result of the interplay of repulsion and magnetic interaction between particles.

In the present contribution, we consider assemblies of cubic magnetic particles and analyze the structural changes of minimal energy configuration. Designing a rational assembly mechanism based on magnetostatic interactions requires understanding differences between the energies of different structures. We systematically investigate clusters and lattices stabilized by magnetic dipolar coupling of their nanocube constituents. We compared the magnetic binding energy to magnitude of repulsive or attractive surface interaction needed to switch between different structures.

**Results**

**Energy of dimer**

**Magnetic energy of cubes in contact**

It is instructive to first consider the interaction between two particles with completely touching faces and compare it with two elementary dipole situation. A ground configuration of the system is head-tail with magnetic energy $u_{001}^{[001]} = 1.63$ eV, see inset in Figure 2(a). Due to symmetry, the magnetic T-configuration in Figure 2(b) has zero energy. 2 This feature is fully consistent with two spherical magnetic bids where magnetic T-configuration also has zero energy. The magnetic energy of the zig-zag configuration for magnetic cube magnetized along principal diagonal is $u_{111}^{[111]} =$

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2Opposite to head-tail configuration would be head-on-head configuration with the positive energy value $u_{001}^{[001]} = 1.63$ eV indicating that there is a strong energy penalty upon assembling a magnetic dimer in that configuration from infinite relative separation.
Figure 2: Different configurations of two uniformly [001] and [111] magnetized cubes. For [001] magnetization, so called, (a) head-tail and (b) T-configuration are shown. In case of [111] magnetization, so called, (c) zig-zag, (d) parallel, (e) head-tail, (f) point and (g) edge configurations are shown.

Figure 3: The total binding energy $u$ profile for a system consisting of a cube moving along the face diagonal of the other one. The magnetization is oriented in the (a) [001] and (b) [111] direction. The uniformly magnetized cubes with $d = 80$ nm side are considered with $M_s = 18$ kA/m magnetization. The energies are given in electron-volts, i.e., the reference magnetic energy is $\nu = 1$ eV. The surface coupling energy of two cubes in full contact $e_s = \varepsilon_{ss} d^2$ is varied. The results are shown without $e_s = 0$, as well as for attractive $e_s = -0.1, -0.2, -0.4$ eV and repulsive $e_s = 0.4, 1, 2, 4$ eV surface couplings.

$2u^{[001]}/3 = -1.11$ eV and for configuration with parallel [111] magnetization has zero energy, both configurations are shown in Figure 2(c) and (d), respectively.
If we include surface energy, the total energy is a result of the net magnetic orientations and the contact surface. For dimer of nanocubes, the assembly mechanism drives the particles to adopt structures that create a head-tail configuration, very much like chains of magnetic beads. In the case of [001] direction, this leads to a deep central minimum of potential energy concerning the lateral movement of the magnetic particles, and consequently to a quite stiff configuration. On the contrary, when the magnetization is along the principal axis, \( i.e., [111] \) direction, the structure becomes more flexible. The landscape has two minimum along diagonal. The configuration with minimal energy has a zig-zag dipole vector placement, \( i.e., \) Figure 2(c), and the system can extend to a full head-tail configuration by relative rotation of the cubes. The head-tail configuration is shown in Figure 2(e) and corresponds to the second minimum of the energy at point \( \Delta r = 0.5d = 40 \text{ nm} \), which corresponds to the center of mass of one particle being placed over the other. At the minimum energy point (zig-zag configuration), the distance between their centres \( \Delta r_2 \) is equal to the cube size \( \Delta r_2 = d = 80 \text{ nm} \) and particles are fully in contact, cf., Figure 2(c). A second minimum, the centres of mass of the particles are 22\% further apart then at global minimum (as shown in Figure 3, \( \Delta r_2/d = \sqrt{3}/2 \), \( i.e., \) \( \Delta r_2 \approx 98 \text{ nm} \) for 80 nm particles). The full head-tail configuration of dipoles has magnetic energy \( u^{[111]}_{ht} = -0.81 \text{ eV} \), which is 27\% energy increase compared to global minimum and the particles touch only with a quarter of the surface, cf., Figure 2(e).

Finally, we want to find out what is the lowest energy configuration of the two cube system if there is no contact surface? Figures 2(f) and (g) show two [111] magnetized cubes touching only in a point or over an edge. The head-tail magnetic configuration in Figure 2(f) has \(-0.25 \text{ eV}\) magnetic binding energy. The cubes touching over the edge have zig-zag magnetic configuration and a slightly lower binding energy \(-0.28 \text{ eV}\).

**Energy contribution of contact surface**

Now we analyze the evolution of energy profile along the cube’s face diagonal connecting two minima. The results are shown for different, so-called, surface coupling energies of two cubes.
in full contact $e_s = \varepsilon_s d^2$. We use surface coupling energy rather than energy per surface area to facilitate comparison with magnetic energy. If the particles attract each-other, \textit{i.e.}, for $e_s < 0$ the global minimum becomes more pronounced since attraction promotes fully touching configuration of the cubes (maximal contact surface). This leads to a deeper central minimum of the potential energy and consequently to increased stiffness of the configuration to any kind of deformation. If the surface interaction is repulsive, \textit{i.e.}, for positive $e_s > 0$, the energy minimum becomes shallower. In the repulsive regime, two magnetic configurations start to behave strikingly differently. For $e_s > 0$, the central minimum of [001] disappears and evolves into a potential valley with local conical energy maximum in the middle, see Figure [3]. With increasing repulsion, the maximum increases, the stable configuration moves towards the edge of [001] magnetic nanocube and becomes fully unstable for $e_s \gtrapprox 2$ eV, \textit{i.e.}, particles will not stay in close contact. The [111] magnetic particles will stay in contact even for very large repulsion energies, \textit{i.e.}, $e_s \approx 4$ eV.

For [111] magnetic nanocubes surface energy determines the magnetic configuration. The critical surface repulsion energy is equal to difference of magnetic energies of two minima $\varepsilon_S^{crit} = u^{[111]}_h - u^{[111]}_z \approx 0.3$ eV. Below $e_s = 0.3$ eV particles will tend to stay in zig-zag magnetic configuration, and above they will open up to the head-tail configuration. Due to a head-tail configuration, the nanocubes will stay in contact even for surface repulsion $e_S = 2$ eV, \textit{i.e.}, two times the maximal magnetic binding energy the cubes.

**Minimal magnetic energy assemblies**

**Magnetization [111]: from polymorphs to super-cubes**

We have investigated ground state configurations of nanocube assemblies $2 \leq N \leq 8$ by calculating energies of all possible magnetic and geometrical arrangements. The diagonal polarisation of [111] magnetized cubes results in a strong tendency to create closed flux structures. The two-dimensional polymorphs were ground states only for $N = 3, 4$, c.f. Figure [4](A1) and (B1). For $N \leq 5$, three-dimensional polymorphs become ground state with uncompensated magnetic moment for $N = 5$, see Figure [4](C1). Interestingly, the formation of five particle polymorph leads to penalty (increase)
in magnetic binding energy, \textit{i.e.}, binding energy per particle increases from $u_4 = -1.16$ eV to $u_5 = -1.06$ eV. Also we should note that there is less then 1\% binding energy difference for $N = 5$ and 6 polymorphs between 3D (\textit{e.g.}, ground state) and 2D (non-ground state isomer) structures, \textit{e.g.}, $u_5 = -1.06$ eV for the cube on top of the $2 \times 2$ square and $u_5 = -1.05$ eV on the side, see in Figure 4E1 and (F1), respectively. Further closure of head-tail magnetic circulation of all magnetic cubes, \textit{i.e.}, for $N = 8$, leads to 10\% difference in magnetic binding energy between 2D and 3D structures. More specifically, for polymorphs, a well-known arrangement of the dipoles in head-tail circulation is found (see Figure 4). Direct computation of energies for all possible configurations increases exponentially with the number of cubes so, beyond eight nanocubes this approach is not feasible. For a super-cube of composed of $3 \times 3 \times 3$ nanocubes, \textit{e.g.}, $N = 27$, the
minimal binding energy was obtained by genetic algorithm^{21} (see Supplementary Information).

All three dipole vector components along sides of the cubes are inscribed antiferromagnetically (cf., \( N = 8 \) in Figure 4), resulting in a vortex magnetic structure. With the increasing number of magnetic cubes, the binding energy of super-cube is converging to a value of \( u_{\infty} = -2.68 \) eV with power exponent \( N^{-1/3} \).

In the following section, we will demonstrate that antiferromagnetic magnetization is characteristic of dense systems of magnetic cubes independent of magnetic anisotropy.

**Magnetization [001]: from chain to rods**

The computational cost of the search for the ground states is greatly reduced when we study [001] magnetization along one side of the cub. The chains have minimal binding energy for \( N \leq 9 \). Beyond \( N = 9 \), we observe different behaviour for even (i.e., \( N = 2k, k \in \mathbb{N} \)) and uneven number (\( N = 2k \)) of particles. For an even number of particles \( 10 \leq 2k \leq 14 \), a ribbon composed of two chains is created, see Figure 6(A2). The configuration is antiferromagnetic, i.e., the two chains have magnetization. At this point, energy increase due to breaking one chain into two is offset by the magnetic interaction of the resulting two touching chains. This configuration is followed by a three-dimensional rod with a square \( 2 \times 2 \) profile between \( 16 \leq 4k \leq 124 \), cf. Figure 6(D2). For an uneven number of particles the chains remain stable until \( 2k + 1 \leq 15 \), see Figure 6(C2). Beyond this point, two touching chain configuration, with \( k \) and \( k + 1 \) particles becomes energetically favorable. The reason for this is a penalty of the ultimate particle, having only one neighbor, compared to the double chain composed of an even number of particles. As a result, the assemblies with unequally long chains exhibit higher binding energies and retarded transition to thicker rods. A further example is a transition from the double chain with \( 4k + 2 \) particles to a square-profile \( 2 \times 2 \) rod. This transition is taking place at \( 4k + 2 \leq 36 \). The energy differences between competing states are quite small (less than 1% total energy) and also much smaller than the gain in binding energy due to the additional particle.

For simplicity, from now on, we will only consider rods composed of chains with equal length
Figure 5: Magnetic binding energy per particle ($u_N$) as a function of number of cubes ($N$) in polymorphs (dots), super-cubes (dashed), super-spheres (full line) for magnetized cubes along the main diagonal ([111] direction) and minimal energy super-rods with [001] magnetized cubes. Regular isomers of super-structures are shown for $N \approx 350$ and 1000 constituent nanocubes. The uniformly magnetized cubes with $d = 80$ nm side are considered to have $M_s = 18$ kA/m magnetization. The energies are given in electron-volts, i.e., the reference energy is $\nu = 1$ eV.
Figure 6: Magnetic energy per particle \( (u_N) \) as a function of number of cubes \( (N = 8, 10, 15, \) and 16) with magnetization in the [001] direction. The ground state structures (left) and examples of non-ground state isomers (right) are shown. The uniformly magnetized cubes with \( d = 80 \) nm side are considered with \( M_s = 18 \) kA/m magnetization. The energies are given in electron-volts, \( i.e., \), the reference energy is \( \nu = 1 \) eV.

and analyze the evolution of the profile of the rods. We observe an almost smooth energy drop, see Figure 5. This is reminiscent of behavior seen in rods composed of magnetic spheres.\(^{21,22}\) For \( N = 350 \) magnetic nanocubes, we obtain \( 5 \times 5 \times 14 \) and for \( N = 980 \) \( 7 \times 7 \times 20 \) rods. The binding energy of the rods converges to \( u_{3D,[001]}^\infty = -2.68 \) eV, \( i.e., \), which is the same energy already found in the super-cubes of \( [111] \) magnetized particles.

**Dependence of structure on surface interaction**

**Attractive surface coupling: super-cubes vs. super-spheres**

At this point, we would like to discuss the situation when the surface coupling is attractive and much stronger than dipolar magnetic interactions between nano-cubes. This is a limiting case where system behavior is independent of magnetic anisotropy (in our case, [111] or [001]). When the surface coupling is attractive, \( i.e., e_s < 0 \), the assemblies tend to decrease total (free) surface
area. One can construct, so-called, super-sphere in which magnets are centered around the middle of super-sphere within a radius $R$ (cf. Figure 5 and supplementary movie). Due to the discrete nature of super-sphere, its surface ($S_{ss}$) to volume ($V_{ss}$) ratio is 23% larger, i.e., $S_{ss}/V_{ss} \approx 7.4N^{-1/3}$, for $N \gg 1$, than that of the equivalent super-cube, $6N^{-1/3}$. This means that the creation of a super-cube (rather than a super-sphere) is a path to reduce free surface in a system composed of nanocubes.

In Figure 5, we have numerically compared the magnetic binding energy $u_N$ (per particle) of super-spheres and super-cubes. To calculate magnetic energy, the super-cubes and spheres were inscribed antiferromagnetically with [111] magnetization. We wanted to demonstrate that also with the respect to magnetic binding the super-sphere is an unfavorable configuration. The resulting energy evolution with the number of nanocubes is displayed in Fig. 5. The energy of a super-sphere is always above the energy of a super-cube (except in case of the smallest the sphere, i.e., $N = 8$, which is also a cube).

**Phase behaviour of [111] magnetized nanocubes**

In Figure 7, we study the evolution of arrangements of [111] magnetized nanocubes with the strength of repulsive surface interaction. We start from minimal magnetic energy structures described in the previous section and analyze the difference in energy resulting from the surface coupling between particles, i.e., $e_s = \epsilon_{ss}d^2$. When the surface repulsion increases $e_s \gtrsim 0.5$, the magnetic assemblies tend to increase surface area. The polymorphs formed only of a few particles (i.e., $N < 27$, the grey area in Figure 7) will transcend directly into chains with partially touching cubes and head-tail magnetic configurations. This is somewhat surprising since the chains with fully touching faces higher binding energy. Nevertheless, four times smaller contact surface of partially touching head-tail magnetized cubes makes them win as minimal energy state over fully touching chains. The limiting energies are denoted with (green) squares in Figure 7. For surface repulsion coupling $e_s \gtrsim 0.6$, we observe a transition to, so-called, corner-cube structures.

This remarkable transformation to corner cube structures originates from the necessity to avoid
Figure 7: Phase diagram of magnetic cubes, with a surface coupling $e_s = \varepsilon_s d^2$, plotted as a function of the cluster size. The (green) squares, connected as a guide to the eye, represent polymorphs being comprised only of a few particles ($N = 4, 5, 6, 7, 8, 12, 16, 18$) located in the grey area which transcend directly into the chains of partially touching cubes with head-tail magnetic configurations. The (red) circles denote upper limit of stability of head-tail chains above which they transform into corner-cube 2d structures. The right side of the diagram follows the phase transformation of large structures ($N \geq 27$). The nanoparticles are arranged in super-cubes configurations for attractive surface interactions. The dotted (blue) curve represents the repulsive regime phase boundary between elongated tilted super-rods and super-cubes. The super-rods transform first into chains of partially touching particles with increasing surface repulsive coupling (full curve). For strong repulsive coupling, we observe the formation of corner-cube structures (dashed curve). The uniformly magnetized cubes with $d = 80$ nm side are considered to have saturation magnetization $M_s = 18$ kA/m. The energies are given in electron-volts, i.e., the reference energy is $\nu = 1$ eV.

surface contact while simultaneously increasing binding energy by minimizing the distance between cubes. The transition from $4 \times 4$ square to corner-cube square takes place for a surface coupling energy of $e_s = 0.84$ eV. Figure 8 gives an overview of corner-cube 2D structures. The constitutive chains have the magnetization parallel to the patch longer side and ferromagnetic configuration. The magnetic binding energies are considerably higher than in the case of polymorphs, $u_{4\text{cc}}^c = -0.32$ eV, $u_{12\text{cc}}^c = -0.32$ eV, and $u_{32\text{cc}}^c = -0.62$ eV, see Figure 8.

We will show now, how the pattern observed for polymorphs evolves for larger structures ($N \geq 27$). Attractive surface coupling $e_s < 0$ stabilises super-cubes. By tuning repulsive surface coupling ($e_s > 0$), the super-cube can increase surface in two ways; (i) by increasing surrounding
surface making nanocubes oblique to super-structure, and (ii) elongating the structure as a whole into a super-rod. The critical repulsive surface coupling energy depends on the size of these assemblies, see the dotted (blue) line in Figure 7. When the number of nanocubes exceeds roughly $10^3$, the difference between super-cube and super-rod made of tilted nanoparticles particle becomes less than 25 meV per particle (which corresponds to the thermal energy of individual cubes at room temperature). Therefore, the presence of a small additional repulsive interaction between particles might explain the experimentally observed ribbons of $45^\circ$-tilted nanocubes, cf. Ref. 6 and Figure 1F,G. It is reasonable to expect that surface repulsion would lead to the creation of chains (e.g. seen in Figure 1D) with partially touching cubes and head-tail magnetic configurations and, indeed, they represent intermediate structure to corner-cube structures, cf. dashed curve in Figure 7. Still, for a large number of particles, i.e., $N > 125$ the chain vanishes as an intermediate structure and direct transition to corner-cube structures takes place, cf. Ref. 20 and I, H, J. With an increasing number of magnetic cubes the binding energy of the corner-cube structure is converging to
value of $u_{2D,cc} = -0.91$ eV. This binding energy is only about 30% of the value for bulk magnetic cube structure, i.e., $u_\infty = -2.68$ eV. The resulting limiting surface energy required to unrolling super-cube into a corner-cube surface converges to $e_{cc}^{[111]} \approx (e_{corner}^{[111]} - e_{2d,cc}^{[111]})/3 = 0.59$ eV, cf. in Figure 7).

Figure 9: The phase diagram for magnetic [100] nanocubes with a surface coupling $e_s$ plotted as a function of the cluster size $N$. The (blue) squares, connected as a guide to the eye, represent transition from super-rod to regular super-cube for $N = 8, 27, 64, 125, 216, 343, 512, 729,$ and $1000$. The dotted blue line is trend from the energy scaling laws for energy of super-rods and super-cubes. The dashed (orange) curve is upper limit of the the stability of super-rods above which they transform into head-tail chains. The dash-dotted (red) curve represents the limit of stability of the chains. The uniformly magnetized cubes with $d = 80$ nm side are considered to have saturation magnetization $M_s = 18$ kA/m. The energies are given in electron-volts, i.e., the reference energy is $\nu = 1$ eV.

**Phase behavior of [001] magnetized nanocubes**

In Figure 9, the diagram shows boundaries for the number of building blocks and the surface interaction energy between different classes of structures build with [001] magnetized nanocubes. The repulsive surface interaction at which [001] super-rods remain stable increases with the number of cubes. For $N > 100$ nanocubes, super-rods remain stable for $e_s < 0.3$ eV. The energy of infinite chain is $u_{\infty,chain}^{[001]} = 2.01$ eV and rod composed of [001] nanocubes will eventually converge to $u_{\infty}^{3D} = 2.68$ eV. Therefore, the limiting surface repulsion energy necessary to prevent creation of
very large three dimensional agglomerates is $\varepsilon_{S}^{[001]} = (u_{\infty}^{3D} - u_{\infty}^{\text{chain,[001]}})/2 \approx 0.33$ eV. As we already discussed, super-rods have larger surface energy than super-cubes. The surface attraction will tend to reduce the surface, i.e., creating super-cubes, cf. $\varepsilon_{S} < 0$ in Figure 9. Based on scaling laws for [001] super-cubes and rods we estimate that the critical surface attraction is given by $\varepsilon_{S} = -0.6$ eV for $N \gg 1$.

**Discussion**

The competition between shape and magnetic anisotropies offers various pathways for self-assembly. To explore the structure of polymorphs ($N \leq 27$), analytic calculations are combined with a systematic search for ground states. Two orientations of the dipole relative to the cube geometry were considered, namely in the crystallographic directions [001] and [111]. For magnetic anisotropy in the [001] direction, linear chains have minimal binding energy for $N \leq 9$. Beyond $N = 9$, we observe complex re-entrant behavior. Between $10 \leq N \leq 15$, for an even number (i.e., $N = 10, 12, 14$) of particles, the ground state is an antiferromagnetic ribbon, and the structure has a closed magnetic flux. For an uneven (i.e., $N = 11, 13, 15$) number of particles chain remains the ground state and does not enclose the magnetic flux. The strong finite-size effects found in dipolar systems are responsible for the persistence of the chains as the ground state. Beyond $N \geq 16$, three-dimensional antiferromagnetic rods were found as ground states. In the case of [111] magnetized cubes, the ground state was found to consist of structures derived from a simple square lattice resulting in the super-cubes seen in experiments, cf. Figure 1E. The surface minimization and the interplay of magnetic anisotropy and cube geometry, which in turn form antiferromagnetic alternating magnetic order, are the driving mechanisms leading to the formation of the super-cube.

The creation of directed non-close-packed arrangements is a technological challenge. We depart in our consideration from ground-state configurations found in polymorphs ($N \leq 27$) and compare them with configurations found in experiments. We study the transition between different states with increasing repulsion surface energy. For magnetization [001], the linear chain
becomes minimal energy state for a repulsive surface coupling energies higher than 22% magnetic bulk binding energy. The [111] magnetized cubes will transit into a chain structure only in a narrow range of surface repulsive energies and for small and intermediate number of constitutive particles $N < 200$. The limit of stability of compact three-dimensional structures lies also around 60% of the magnetic binding energy of the cubes. The strong repulsion still does not result in the fully stretched chains with cubes touching only at the corners. Instead, the system collapses into a corner-cube two-dimensional configuration with the cubes in contact over the edges. Surface coupling, repulsive or attractive, has a profound influence on the magnetic order of the assembled structures. Dense configurations, such as super-rods or super-cubes, are antiferromagnetic, while non-close-packed arrangements, such as chains and corner-cube planes, are ferromagnetic.

The results revealed vanishing differences in the binding energy between different super-structures, cf., in Figure 5, due to the insertion of additional nanocubes or between different isomers. Even for the smallest considered assemblies - polymorphs containing only several particles (cf., Figures 4 and 6), these differences in energy per particle were comparable to the thermal fluctuations at room temperature. Such a small difference in energy can result in the formation of the non-ground state structures seen in the experimental realization of polymorphs. The probability of proliferation of non-ground state structures decreases with the magnitude of the energy difference between non-ground states and the ground state. In the case of the super-structures, energy differences due to the addition of a nanocube or between different structures with similar numbers of nanocubes were decreasing with the number of particles following the $N^{-1/3}$ scaling law. Nevertheless, the total energy differences of the structures increase with system size as $N^{2/3}$ leading to the formation of fairly regular super-structures such as super-cube, super-rods, or corner-cube structures.

**Conclusion**

We demonstrate a rich variety of structures and non-close-packed arrangements that can be engineered from nanocubes with a combination of surface interaction and magnetic dipole-dipole
coupling. Our results are in good agreement with the experimentally obtained structures. The model studied here approaches systems where interparticle energies of interaction are much higher than the thermal energy of the particles. In most of the structures, particles assemble forming flat surfaces to avoid getting trapped in local minima. We established the relationship between arrangement, magnetic anisotropy ([100] and [111]), surface interaction, and size of the system. The results are scalable and our approach is valuable to research aimed at the application of novel magnetic superstructures and to direct the self-assembly of unique structures at different scales. The directed assembly of structures opens up new possibilities in material science in terms of tuning properties through the balance of surface and magnetic interactions, which is of practical relevance in many areas of research, including biomedical materials, energy applications, and complex nanoarchitectures for metamaterial coatings or plasmonic elements.

Model

Dipolar magnetic interaction

Magnetic cuboids were synthesized from iron and its oxides, as well as from non-ferrous materials with different magnetic anisotropy and remanent magnetization, i.e., direction of magnetic moment relative to cube’s geometry and magnetization remaining after an external field is removed, respectively. An overview of sizes, saturation magnetization, and easy magnetization axis found in literature is given in Tab. 1. Magnetite (Fe₃O₄), nickel platinum alloy, nanocubes magnetic easy axis lying along the [111] crystallographic direction. This is in contrast to cubes of iron FePt and cobalt/zinc ferrite that have cubic magnetic anisotropy and therefore preference for magnetization along [001] direction. An additional variability of the properties may be achieved with core-shell structure, which can combine high remanent magnetization of the core with magnetic anisotropy defined by the shell. The iron-oxide nanocuboids (i.e., hematite, and magnetite) can be synthesized as micron-sized colloids. Hematite colloids, in particular, maintain a permanent dipole moment even at large particle size.
Table 1: Mean size, saturation magnetization ($M_s$), and easy magnetization axis for different materials found in literature.

| nanocube       | size [nm] | $M_s$ [kA/m] | easy axis | reference          |
|----------------|-----------|--------------|-----------|--------------------|
| FePt           | 9         | 0.8          | [001]     | Chen et al.$^{23}$  |
|                | 11.8      | 0.8          |           | Chou et al.$^{24}$ |
| CoFeO$_4$      | 11        | 16           | [001]     | Song and Zhang$^{25}$ |
|                | 20        | 8            |           | Wu et al.$^{26}$   |
| Zn$_{0.4}$Fe$_{2.6}$O$_4$ | 20 | 40          | [001]     | Noh et al.$^{19}$  |
|                | 60        | 50           |           |                    |
| Fe             | 18        | 6            | [001]     | Kronast et al.$^{27}$ |
| NiPt           | 50        | 5            | [111]     | Cuya Huaman et al.$^{20}$ |
| Fe$_3$O$_4$    | 19        | 15           | [111]     | Abenojar et al.$^{28}$ |
| magnetite      | 30        | 13           |           |                    |
|                | 42        | 18           |           |                    |
|                | 106       | 18           |           |                    |
|                | 1000      | 480          |           | Aoshima et al.$^{19}$ |
| $\gamma$Fe$_2$O$_3$, maghemite | 9   | 4            | [111]     | Ahniyaz et al.$^{12}$ |
| $\alpha$Fe$_2$O$_3$, hematite | 1000 | 2.2         | [111]     | Sacanna et al.$^{14}$ |

In this work, small single-domain magnets are treated like uniaxial magnets. Their interaction is described through dipole-dipole interaction potential: it is assumed that each particle carries identical dipolar (magnetic) moment with magnitude $M_0 = M_s d^3$. In this work, we consider the two most common magnetization directions: alongside [001] or along the principal diagonal [111] of the cube. Magnetic nanoparticles can have complex coupling involving both dipolar and exchange interactions.

In case of pure 80 nm$^3$ single-crystal magnetite cube and $M_s = 18$ kA/m, the reference magnetic interaction energy $\nu = \mu_0 M_0^2 / 4\pi d^3$ was estimated to be $\nu = 1$ eV, i.e., $40 k_B T$, where $T = 300$ K is the temperature and $k_B$ is the Boltzmann’s constant. The magnetic field generated by one particle at the c.m. of the other particle (placed side by side) is $B_0 \approx \mu_0 M_0 / (2\pi d^3) = 3.6$ mT.

The dipolar magnetic interactions between an assembly of magnetic cubes are treated semi-analytically for small clusters $N \leq 8$ or using 9-dipole approximation$^{17}$ (see Supplementary Infor-

$^3$We chose the cube’s dimensions to facilitate comparison both with real units used in experiment and scaled used in generic theoretical considerations.
The minimization of energy was done systematically for $N \leq 16$ for all possible geometric and magnetic configurations. For larger systems, the genetic algorithm was used to minimize magnetic configuration (i.e., $N > 16$).

**Surface interaction**

The nanocube assemblies shown a clearly defined contact surface area. These surfaces can be engineered repulsive or attractive, either by adsorbed layers from solution or by polymers grafted on it. The stacking of the cubes tends to reduce or increase the surface area depending on the nature of surface interaction. In our calculations, surface energy is proportional to the contact surface. We will first discuss strong van der Waals attraction of the clean surfaces. Then we will explain how the surfaces can be modified to obtain weak attractive or even repulsive forces, and show that resulting energy scales are similar to that of magnetic interaction.

Clean metallic or metal-oxide nanocubes interact with each other through van der Waals interactions characterized by interaction energy and distance. The interaction energy parameter can be calculated as:

$$\epsilon_{ss} = -A_{mm}\sigma_{mm}^4\rho^2/4\pi^2$$

where $\sigma_{mm} = 0.35$ nm is the size parameter for iron atoms, $\rho = 85$ nm$^{-3}$ the density of iron atoms in the bcc lattice, and $A_{mm} = 2.38$ eV is the average Hamaker constant for metals. The interaction distance is comparable with the atom size, i.e., $\sigma = 0.3 - 0.5$ nm. We obtain a value of $\epsilon_{ss} = -6$ eV/nm$^2$, which result in a surface binding energy of $e_{ss} = \epsilon_{ss}d^2 = 38.4$ keV over an $80 \times 80$ nm surface (fully touching cubes) and is comparable to the values found elsewhere. In this work, we consider 80 nm particles. As a result, the potential will be extremely short-ranged, i.e., only touching bodies interact. The resulting interaction, which is proportional to the contact surface, will be highly dependent on the orientation of the touching cubes.

Since van der Waals surface interactions are quite strong but short-ranged, so-called steric stabilization is used to control the coalescence of the particles typically by a thin adsorbed or grafted layer of appropriate thickness. These thin layers are used to obtain weak attraction, comparable to magnetic interaction energy between particles, and even repulsion, which can accommodate
the formation of non-close-packed agglomerates. Engineering the repulsion and distance between magnetic particles is a typical way to steer the extent of the cube’s aggregation. The repulsive forces can arise from neutral steric layers (i.e., entropic repulsion of grafted polymer chains) or electric double layers. The excluded volume of steric layers covering two particles results in a repulsive force, i.e., each atom within a layer’s molecule occupies a certain amount of space and if atoms are brought close together, there is an associated cost in energy. The thickness of layers and local density of grafted/attached polymers determines the extent and strength of repulsion, respectively. The maximal energy of the repulsion is of the order of $\epsilon_{ss} = 3 \text{ meV/nm}^2$, i.e., $\epsilon_s = 19.2 \text{ eV}$ for 80 nm particles, cf. Ref.94. We should also note that while the interaction between surfaces is repulsive, the grafted-polymer chains can accommodate edge contact. Gao et al.9 find weak and extremely short-ranged attractions between edges, which we did not include in our model. These edge-edge and edge-surface interactions will certainly further stabilize open structures analyzed in the present work.

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Supporting Information Available

The following files are available free of charge.

The Supporting Information is available free of charge on the ACS Publications website.

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4The interaction is repulsive with a distance of about 5 nm for the grafting density of 0.04 chains/nm².
Analytic expressions for magnetic field of [001] and [111] uniformly magnetized cubes; Energy calculations; Discrete dipole model for interaction of magnetic cubes; Genetic algorithm.

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