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Supporting Information

Self-Organization in Dipolar Cube Fluids Constrained by Competing Anisotropies

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1 Colloidal system

1.1 Hematite cubes properties

Micrometer sized magnetic hematite colloids are prepared via forced hydrolysis of iron(III) chloride solutions as described in the Methods section. To exclude the presence of iron oxide impurities that could contribute to the overall magnetic properties of the particles, we performed XRD (Figure S1(a)) and Curie balance measurements, confirming that the particles are composed exclusively of hematite. From magnetization curves (see Figure S1(b)) we find a magnetic moment per particle of about $\mu_{exp} = 2.8 \times 10^{-15} Am^2$ for hematite cubes with edge length 1135 nm. This value is about 8% higher than the calculated moment ($\mu_{calc} = 2.6 \times 10^{-15} Am^2$) assuming a spontaneous magnetization of $M_{s,hem} \approx 2.2 \times 10^3 Am^{-1}$ for cubes of equivalent size.

XRD measurements were performed on dried hematite at room temperature on a Bruker-AXS D8 advance powder diffractometer, using Co K $\alpha_{1,2}$ radiation ($\lambda = 1.79026$ Å). Peak positions were compared to the International Centre for Diffraction Data (ICDD) database.

Magnetization curves of hematite cubes were measured with a Micromag 2900 Alternating Gradient Magnetometer (AGM, Princeton Measurements Cooperation). Measurements were performed on a known amount of dried hematite samples. The dipole moment per particle, μ_p , was measured using $\mu_p = \frac{Mr}{fN}$, where Mr is the remanent magnetization and f is a factor (0 < f < 1) that accounts for the alignment of the dipoles

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in the sample, here we used f = 0.5 assuming the particles are all oriented randomly in the 3D sediment.



Figure S1: (a) Typical magnetization curves from Alternating Gradient Magnetometer measurements for a sediment of randomly oriented hematite cubes. (b) X-ray (powder) diffraction pattern of bare hematite cubes confirming the composition of the particles.

2 Interaction energy

2.1 Double Layer Repulsion

Double-layer repulsions between the silica coated hematite cubes were calculated using:

$$U_e = \frac{2\sigma\Psi_0}{kT} L^2 e^{-\kappa x},\tag{S1}$$

where Ψ_0 is the surface potential (50 mV from electrophoresis measurements), L is the edge length of the cube, x is the separation between the cubes, $\kappa^{-1} = 3$ nm is the Debye length calculated for a sodium chloride concentration of 10 mM, and σ is the surface charge defined as: $\sigma = \frac{2\epsilon\epsilon_0 kT}{e}\kappa \sinh \frac{e\Psi_0}{2kT}$, where ϵ_0 is the vacuum permittivity $(\epsilon_0 = 8.854 \times 10^{-12}C^2N^{-1}m^{-2})$, ϵ is the dielectric constant of the medium, in this case water, and e is the elementary charge.

2.2 Dipole-dipole interaction strength

Even in zero-field environment dipolar structures formed by hematite cubes form flexible but quite strong bonds: single particles are rarely seen for samples at equilibrium, even at low particle concentrations, and we never observed single particles disconnecting from clusters suggesting a relatively strong binding energy on the order of at least several k_BT . To estimate the magnetic interaction between two magnetic cubes we used:

$$U_d = \left(\frac{\vec{\mu_1} \cdot \vec{\mu_2}}{r^3} - 3\frac{(\vec{\mu_1} \cdot \vec{r})(\vec{\mu_2} \cdot \vec{r})}{r^5}\right)\frac{\mu_0}{4\pi kT}$$
(S2)

where μ_0 is the vacuum permeability ($\mu_0 = 4\pi \times 10^{-7} J A^{-2} m^{-1}$), μ_1 and μ_2 are the dipole moments of the two interacting particles, in our case $\mu_1 = \mu_2 = \mu_{p,exp} = 2.8 \times 10^{-15} Am^2$, and r is the centre-to-centre particle distance.



Figure S2: (a) Computer generated model of a cube with m = 4, where the white arrow indicates the direction of the dipole moment lying on the plane perpendicular to the c-axis (blue). We assume the dipole moment to form an angle of $\alpha = 19^{\circ}$ with the closest internal diagonal [111] of the cube. (b) Dependence of the center-to-center distance (r) on the mutual angle ϕ for two cubes (edge length 1135 nm coated with a 100 nm thick silica layer and m = 4) exploring all possible orientations in the plane.

2.3 Total interaction

We can estimate the total interaction energy between two cubes (dimer) confined in 2D by adding dipolar attractions Equation S2 and the shorter-range repulsive double layer contributions Equation S1 that arise from charged silica surfaces in water. To predict the ground state structure of two neighboring dipoles in a dimer, we have calculated all possible relative dipolar orientations for two cubes (Figure S2(b)) with 1135 nm edge length coated with an amorphous silica shell 100 nm thick, with shape parameter m = 4 and a dipole moment per particle $\mu_p = 2.8 \times 10^{-15} Am^2$. The dipole moment was chosen to be at a tilt angle of $\alpha = 19^{\circ}$ toward the face of the cube to reflect the bulk magnetic properties of hematite as shown in Figure S2(a). From the calculations in Figure S3 we found that the maximum dipole-dipole interaction is obtained when the dipoles are arranged in a zig-zag configuration as shown in the inset of the bottom-left plot. This minimization is only valid for 2D systems where a dimer consists of two cubes in a face-to-face configuration.

The plot in Figure S4(a) shows the total interaction potential $U_{tot} = U_d + U_e$ (orange) as the sum of dipolar attractions U_d (blue) and double-layer repulsions U_e (purple) between two cubes confined in 2D. The maximum attraction at contact is on the order of ~90 k_BT. Growing an amorphous silica shell around the particles allows us to tune the total interaction potential by effectively increasing the distance between the dipoles and therefore decreasing dipolar attraction. The plot in Figure S4(b) shows the total interaction potential curves for magnetic cubes coated with 100, 200 and 300 nm silica shells.



Figure S3: Dipole-dipole interactions between two magnetic hematite cubes with shape parameter m = 4 and dipole moment per particle $\mu_p = 2.8 \times 10^{-15} Am^2$ oriented at a 19° angle with respect to the 111-direction.



Figure S4: (a) Double-layer repulsion (purple), magnetic attraction (blue) and total interaction potential (orange) curves for silica-coated colloidal cubes with edge length 1135 nm and 100 nm silica coating dispersed in aqueous 10 mM sodium chloride solutions. The curves were calculated for cubes approaching with parallel faces with the highest attractive energy assuming dipoles pointing with a 19° angle with respect to the 111-direction as shown in the bottom right corner of the graph. (b) Effect of the silica shell thickness on the total interaction potential.

3 Magnetic field measurements

3.1 Magnetic field setup

Brownian dipolar colloids have the remarkable property to form aggregates, even in the absence of an applied field when their interaction can overcome thermal fluctuations. However, significant interactions with the Earth's magnetic field can also occur when the particle's dipole moment is strong enough ($\mu_p = 1 \times 10^{-15} Am^2$ for an interaction of about 10 k_BT). For our hematite cubes, with $\mu_{p,exp} = 2.8 \times 10^{-15} Am^2$ and $L = 1.1 \ \mu m$, the magnetic interaction energy between the particles and the Earth's field, which varies between about 0.02 mT and 0.06 mT depending on the location on Earth, was calculated using $U_{p,E} = -\mu_{p,exp}B_E$, where B_E is the Earth's magnetic field at the location where we carried out the experiments. On average, we find an interaction energy between our particles and the Earth's magnetic field on the order of 27 k_BT, strong enough to observe Earth-field induced particle and chain alignment, and to inhibit formation of rings and other zero-field structures.

To study magnetic structures formed by cubes in zero and applied magnetic field, precise control of the applied field is required, both in magnitude and in direction. For this purpose we built a set-up using three sets of orthogonally oriented Helmholtz coils, as shown in Figure S5. The plastic support was 3D-printed to allow precise positioning of the set-up inside the optical path of our inverted optical microscope, and the coils were manually winded. The setup and microscope were designed to screw together so that the eye of the objective, and therefore the part of the sample imaged, was always at the center of the coils, where the magnetic field is uniform. The current applied to each set of Helmholtz coils can be precisely controlled electronically and a maximum of about 3 A can be independently applied to each separate couple of coils. The maximum magnetic field that can be generated by this magnetic setup is about 18 mT in the z-direction

and 1.3 mT in the x- and y-direction. Before imaging, the particles were exposed for a short time to a strong field (18 mT) in the z-direction, which uniformly distributes particles throughout the sample. After removal of the z field we can then observe dipolar assembly of the colloids. This process was repeated every time new settings (different field directions or intensities) were applied to the sample.



Figure S5: (a) Custom-made magnetic setup used to control the magnetic field during optical microscopy experiments. The three sets of coils used to control the magnetic field in the x-, y- and z-directions are indicated by the arrows. (b) The magnetic setup is situated around the objective of the inverted optical microscope and it is screwed at the bottom of the objective. This configuration ensures not only the reproducibility of the measurements, but also that the sample (as indicated by the central arrow) is always in the center of the setup, where the magnetic field is uniform.

3.2 Tracking of magnetic structures

Our cubic particles can be tracked to perform quantitative studies on dipolar structures. Since we are dealing with cubic-like particles, we have to optimize the tracking routines. Here, single cubes, isolated or as part of a chain or structure, are identified using a circular Hough transform. This recognition procedure is possible because the edges of the particles imaged by optical microscopy are hazy and their central part is brighter due to light reflection by hematite; it is therefore possible to overlap the shape of the particles with a circle. Figure S6(a) shows part of a typical image used for the tracking of small cubes in the presence of the Earth's magnetic field.

After all particles are identified, the software caches information on the radius and position of each particle. The information is used in the third step to identify particles close enough to be part of the same cluster. In Figure S6(a) each cluster is identified by a red dot. The tracking procedure is repeated for all the frames in a movie of over 600 frames (the intervals between the frames changes depending on the information needed) and the information on the length and angle of each chain is extracted in the form of an angular histogram. An example of angular histogram obtained by tracking chains of cubes in the presence of the Earth's magnetic field, can be seen in Figure S6(b).



Figure S6: Original microscope image used for tracking (a). The center and the radius of every particle are recognized using a Hough circle transform and chains are identified from particles that are close to each other. The whole tracking process is repeated for a large number of frames (more than 600) to account for fluctuations, and the final direction of each chain is computed in an angle histogram (b) that shows the average preferential orientation of the chains. (c) Schematic representation of the vectors involved in the measurement of direction and magnitude of the Earth's magnetic field (\vec{b}).

3.3 Procedure for cancelling the Earth's magnetic field

Cancelling the Earth's magnetic field accurately and reproducibly is not trivial. Every microscopy set-up is different and located at different orientation with respect to the Earth's field lines; in addition, there might be other elements in the surroundings of the microscope that produce a magnetic field, effectively disturbing the measurements. Because the Earth's field is very weak (typically between 0.02 mT and 0.06 mT) and easily influenced by, for instance, electronics in the surrounding, applying a Gaussmeter probe is not an option. We have developed a technique to precisely cancel the Earth's magnetic field (or any other residual field) using our colloidal particle as "probes" for the determination of the strength and direction of the magnetic field lines. When hematite particles are exposed to the Earth's magnetic field, they form chains that align parallel to the field lines. If we consider a scenario where the applied field (\vec{B}) is zero (Figure S6c, left) then the chains align parallel to the Earth's field which form an angle θ with the applied field. To generalize the procedure, we assume that θ is unknown.

If we consider as a reference frame the plane formed by the applied field and its perpendicular direction, then by definition $-\frac{\pi}{2} < \theta < +\frac{\pi}{2}$, as shown in Figure S6(c). The Earth's field vector \vec{b} can therefore be written as:

$$\vec{b} = \begin{pmatrix} \vec{b}cos\theta\\ \vec{b}sin\theta \end{pmatrix}$$
(S3)

When the applied field is not zero, the chain of particles align in a direction that is the sum of the applied field \vec{B} and the Earth's field as shown in Figure S6(c). The total field that the particles experience is:

$$total \ field = \begin{pmatrix} \vec{B} + \vec{b}cos\theta\\ \vec{b}sin\theta \end{pmatrix}$$
(S4)

Because we know the direction and magnitude of the applied field \vec{B} the angle ϕ can be written as:

$$tan\phi = \frac{\vec{b}sin\theta}{\vec{B} + \vec{b}cos\theta} \tag{S5}$$

The angle θ can be experimentally measured and the field applied \vec{B} is known, this equation can therefore be solved for \vec{b} , a vector that represent both magnitude and direction of the Earth's field.

4 Bond Angle Analysis and Kinking Criterion

In order to extract kinked conformations from simulation, a strict kink criterion is required. To that end, we considered only chain structures; we aimed to isolate all kinked chains in the system and neglect clusters with three-fold, and higher, coordinated particles. We extracted all the bond angles ϕ along the length of identified chain clusters, from which we constructed the probability density function, $f(\phi)$. In the interest of a further dipole orientation comparison we performed this bond angle analysis for the two additional dipole orientations as well, further emphasizing the uniqueness of the face tilted orientation. The $f(\phi)$ for each dipole orientation are plotted in Figure S7 ordered as face-tilted, [111], and edge-tilted, from top to bottom respectively. One should note the use of a log-scale for $f(\phi)$. The pink regions of the plots are the bond angle histograms binned according to the Freedman-Diaconis rule. These distributions were fit to a bimodal normal distribution of the form:

$$N(\bar{\phi}_1, \sigma_1^2, \bar{\phi}_2, \sigma_2^2) = aN(\bar{\phi}_1, \sigma_1^2) + bN(\bar{\phi}_2, \sigma_2^2)$$
(S6)

where $N(\bar{\phi}_i, \sigma_i^2) = e^{-(\phi - \bar{\phi}_i)^2/2\sigma_i^2}/(2\pi\sigma_i^2)^{1/2}$ with mean $\bar{\phi}_i$ and variance σ_i^2 ; *a* and *b* are pre-factors, which determine the mixing of the distributions. The bimodal distribution fits are depicted in Figure S7 as blues curves; the component unimodal distributions are shown as the green curves in the upper plot simply to illustrate the kink definition we

have used and shall define shortly. On first inspection, these angular distributions closely reflect the snapshot comparisons we made earlier, the dipolar orientations [111] and edgetilted are extremely similar, whilst the face-tilted orientation is completely distinct. Each distribution is characterized by two maxima; for [111] in the middle plot these maxima are similar in height, a fact that must stem from the high symmetry of this orientation. The maximum at $\sim 180^{\circ}$ corresponds to linear chain segments and the second maximum to the neighbor-to-neighbor offset that can occur along the chains. Similar behavior is seen for the edge-tilted orientation, where a slight preference for linear segments has developed indicated by the increase in height of the $\sim 180^{\circ}$ peak, this reflects the reemergence of extended chain structures due to the dipolar tilt. Focusing on the upper plot, the orientation of primary interest, we find in contrast to the lower two plots one distinct global maximum at bond-angles ($\sim 180^{\circ}$) indicating a marked preference for linear chain segments, whilst the significantly lower local maximum corresponds to the kink chain segments that we have observed. We chose to define the boundary between linear and kinked chain segments as the intersection point of the two constituent normal distributions in our bimodal fit. As indicated on the plot, this angle $\phi_{\rm crit}$ lies at the intersection of the two green curves, the corresponding angle is approximately 157°. Therefore the kink criterion was set as such: any chain cluster containing at least one bond angle less than $\phi_{\rm crit}$ is considered to be composed of at least one kink deformation; clusters with no angles less then $\phi_{\rm crit}$ are considered to be defect free. The most probably kink angle found here, $\phi_{kink} = 143.9^{\circ}$, correlates well with that derived in the manuscript from chain-field orientations.

5 Alternative dipole moment orientations

The experimentally determined dipole moment orientation is found at a 12° tilt from [111] toward the particle face and is confirmed by the striking agreement between experimental observations and simulations. However, to confirm that the specific tilt toward the particle face is indeed responsible for the observed phase behavior, we exploit the ability to re-orient the dipole within the cube in simulations. Specifically, we investigate two different orientations of the dipole: a conventional [111] orientation and an orientation with a -12° tilt angle from [111] towards the particle edge, as shown in Figures S8(a) and S8(e), respectively.

Figures S8(b-d) show the obtained structures for the dipole along the [111] orientation. We find an appreciable difference in the self-assembled structures compared to those in Figure 3 (main text). At zero-field, the structures posses a much more close-packed geometry, with primarily compact agglomerations of four particle rings, which are known to constitute the ground state of such particles. Moreover, chain-like structures observed in the experimental case are not evident. In the weak and strong field regimes there is a complete absence of the kinking phenomenon (Figures S8(c,d). We actually find a scenario where particles are offset along a chain from neighbor to neighbor. Furthermore, one also notices that the structure of the crystalline assemblies is different, appearing to be rather more hexatic in nature. Figures S8(f-h) show the obtained structures for the



Figure S7: Angular probability density functions, $f(\phi)$, of all bond angles in chain structures for the respective systems. Each distribution refers to a different dipole orientation as indicated by the visualization to the left of each plot; the order from top to bottom is face-tilted, [111] and finally edge-tilted. The symbol and curve identifications are given in the legend appearing at the very top of the figure. The histograms are binned according to the Freedman-Diaconis rule. The determined kink criterion ϕ_{kink} and the most probably kink angle ϕ_{kink} , are indicated on the face-tilted plot by the black lines and accompanying annotations.

dipole with a -12° edge-tilted orientation. Here we find a very similar scenario to the [111] dipole, with compact agglomerations at zero-field and a slight offset between nearest neighbors. The only exception arises at zero-field (Figure S8(f)) where chain structures seem to have been stabilized by the re-introduction of the tilt.

Clearly, these two 'incorrect' orientations have markedly more similarities between themselves than with the experimental structures. From this we can conclude that the tilting of the dipole from [111] has a significant effect on the self-assembly protocol active in the system and it matters in which direction this tilt is directed. One can speculate about the significance the size of the tilt angle has. With this in mind, we have included a snapshot (Figure S8(i)) for a system with $\alpha = 19^{\circ}$ (based on the c-axis orientation of hematite) in the strongest field. Kinked structures are still observed, but they are less prevalent and of a slightly different structure to those of $\alpha = 12^{\circ}$. It follows, there can only be a relatively narrow band of face oriented tilt angles for which kinking is observed, which is further supported by the fact that if this tilt angle becomes too large ($\theta \rightarrow 52.5$) the system will tend to a [001] orientation, which will most certainly favor collinear chain configurations.



Figure S8: The dipolar orientation valid for each column of snapshots is indicated in (a) and (e) for [111] and 12° edge-tilted from [111] respectively. (b-d & f-h) Simulations snapshots of cubes with the indicated dipole orientation alongside dipole configurations of selected clusters (insets). (i) Snapshot exploring the effect of an increased face-tilted angle of 19°. Simulation parameters: surface density, $\rho_s^*=0.05$ for (b-d & f-i); Langevin parameters, $\alpha_L^* = 0$ for (b,f), $\alpha_L^* = 18$ for (c,g) and $\alpha_L^*=41$ for (d,h,i); propagation time, $t^* = 5 \times 10^4 \Delta t^*$.

6 Kink formation: an analytical perspective

In the following analysis we are considering individual clusters as isolated entities of given size n. That is to say no assumptions are made about the aggregation of particles to the chain. The equilibrium for this process if highly skewed in favour of association, dissociation is extremely unlikely. When the non-equilibrium nature of the system was discussed in the manuscript, it is in reference to this fact. The treatment in the following section can be viewed in the first instance as athermal and combinatorial. The model considers reconfigurations within chains, where the deformations involved are at a significantly lower energy scale in comparison to bond formation. Thus, the thermal fluctuations, certainly at elevated temperatures, are sufficient to induce changes in state. The thermal component of the problem is introduced implicitly via a fitting procedure at each temperature separately. Whereby, the effects of the thermal agitation are implicitly accounted for.

6.1 Single Chain Partition Function

As a starting point for the following model we posited that the energy of a chain of n hematite cubes $U_k^*(n)$, is the sum of a straight chain contribution $U_0^*(n)$ and an energy penalty term relating to the number of kinks in the chain, k. This is denoted as,

$$U_k^*(n) = U_0^*(n) + k\delta U^*,$$
(S7)

where δU^* is the energy cost of a single kink. Defined in this way we encapsulate all of the kink induced changes in the interparticle interactions along the chain length into δU^* . The straight chain contribution can be described for a chain size n as follows,

$$\beta^* U_0^*(n) = \left[1 - 3\cos^2(\theta)\right] \lambda^* \sum_{i=1}^{n-1} \frac{n-i}{i^3},$$
(S8)

where all pair interactions along the chain are accounted for. Due to the assumption inherit to the model, the explicit dependence of this energy factor cancels out when considering parameters related to probability. The angle θ is equivalent to that defined in the manuscript, *i.e.* the orientation of the chain backbone with respect to the dipole orientations (field direction). This angle is temperature dependent. In doing so, we are assuming that the energy penalty associated with successive kink formation is constant, and independent of the location of a kink along the chain. Furthermore, we are also assuming that multiple kinks in a single chain do not interact with one another. We can write the corresponding *n*-particle chain partition function as,

$$Z(n) = \sum_{k=0}^{n-2} {\binom{n-2}{k}} e^{-\beta^* U_k^*(n)},$$
(S9)

noting that $\beta^* = (T^*)^{-1}$. This summation is over all possible configurations of straight and kinked structures, noting that the maximum number of kinks in a single chain is

(n-2). Substituting for $U_k^*(n)$ and rearranging yields the following:

$$Z(n) = \sum_{k=0}^{n-2} {\binom{n-2}{k}} e^{-\beta^* \left[U_0^*(n) + k\delta U^*\right]},$$

$$= \sum_{k=0}^{n-2} {\binom{n-2}{k}} e^{-\beta^* U_0^*(n)} e^{-\beta^* k\delta U^*},$$

$$= e^{-\beta^* U_0^*(n)} \sum_{k=0}^{n-2} {\binom{n-2}{k}} (e^{-\beta^* \delta U^*})^k$$
 (S10)

In the interest of compactness we made the following identifications: $w_0 = e^{-\beta^* U_0^*(n)}$, the Boltzmann weight of a straight chain configuration, and $w_{\delta} = e^{-\beta^* \delta U^*}$ for the Boltzmann weight of the kink energy penalty. This allows us to write the partition function as,

$$Z(n) = w_0 \sum_{k=0}^{n-2} {\binom{n-2}{k}} (w_\delta)^k.$$
 (S11)

For the final step we turn to the binomial theorem, which for a positive integer N is written in the form,

$$(a+x)^N = \sum_{k=0}^N \binom{N}{k} x^k a^{N-k}.$$
 (S12)

Applying Equation S12 to Equation S11 allows us to write,

$$Z(n) = w_0 (1 + w_\delta)^{(n-2)}.$$
(S13)

6.2 Probability

Having computed the single chain partition function we can now compute the probabilities of the collection of states we are interested in. These are the probability of a straight configuration, $p_0(n)$, and the probability of a chain having at least one kink, $p_{k>0}(n)$. In general the probability for the scenarios such as these can be expressed as,

$$p_k(n) = \frac{w_0 \sum_{k'}^k {k \choose k'} (w_\delta)^{k'}}{Z(n)},$$
(S14)

where k is the maximum kink size under consideration, k' denotes the summation index, the initial value of which depends on the range of kinks considered. For the case of a straight chain the summation disappears as we are only considering k = 0, the probability reduces to,

$$p_0(n) = \frac{w_0}{Z(n)},$$

= $\frac{w_0}{w_0(1+w_\delta)^{(n-2)}},$ (S15)
= $(1+w_\delta)^{(2-n)}.$

For the probability of a chain having at least one kink, given that the following constraint is active,

$$p_0(n) + p_{k>0}(n) = 1,$$
 (S16)

we can trivially read off the probability,

$$p_{k>0}(n) = 1 - p_0(n) = 1 - (1 + w_\delta)^{(2-n)}.$$
 (S17)

This is consistent with Equation S14 for a summation range of $k' \in (1, n-2)$.

6.3 Entropy

With the probabilities of the various states established we can move to an estimation of the entropy of these states. According to the standard statistical mechanical definition of entropy we can write,

$$S^* = -\sum_{i}^{\Omega} p_i \ln p_i, \qquad (S18)$$

where S is the total system entropy, Ω is the total number of microstates of the system, and p_i is the probability of a microstate *i* being occupied. For our system of kinked and straight chains we can recast this as follows,

$$S_{k}^{*}(n) = -\sum_{k'=0}^{k} \binom{k}{k'} p_{k'}(n) \ln [p_{k'}(n)], \qquad (S19)$$

The single microstate probability $p_{k'}(n)$, can be written as,

$$p_{k'}(n) = \frac{w_0(w_\delta)^{k'}}{Z(n)} = \frac{(w_\delta)^{k'}}{(1+w_\delta)^{(n-2)}}.$$
(S20)

Hence, the entropy of the straight chain configurations can be found by considering $S_{k=0}^*(n)$, where no summation is required,

$$S_0^*(n) = -p_0(n) \ln [p_0(n)],$$

= $-\left[\frac{1}{(1+w_\delta)^{(n-2)}}\right] \ln \left[\frac{1}{(1+w_\delta)^{(n-2)}}\right],$ (S21)
= $(1+w_\delta)^{(2-n)}(n-2) \ln (1+w_\delta).$

Whereas for kinked chains we have a slightly more complicated expression, which after a number of algebraic manipulations reduces to the following,

$$S_{k>0}^{*}(n) = -\sum_{k'=1}^{n-2} \binom{n-2}{k'} p_{k'}(n) \ln [p_{k'}(n)],$$

$$= -\sum_{k'=1}^{n-2} \binom{n-2}{k'} \frac{(w_{\delta})^{k'}}{(1+w_{\delta})^{(n-2)}} \ln \left[\frac{(w_{\delta})^{k'}}{(1+w_{\delta})^{(n-2)}}\right],$$

$$= \frac{(2-n)w_{\delta} \ln w_{\delta}}{(1+w_{\delta})} - (n-2) \ln (1+w_{\delta})(1+w_{\delta})^{(2-n)} - (2-n) \ln (1+w_{\delta}).$$

(S22)

At which point we have arrived at an estimation of the entropy for both sets of structure types, which are required for the following section.

Before to moving on, it is beneficial to consider the asymptotic behaviour of these entropy expressions. In the limit of $\delta U^* \to 0$, *i.e.* kink formation incurs no energetic cost, the Boltzmann weight of the kink penalty $w_{\delta} = e^{-\beta^* \delta U^*} \to 1$. Consequently, the entropy contributions reduce to,

$$\lim_{w_{\delta} \to 1} S_0^*(n) = 2^{(2-n)}(n-2)\ln(2), \tag{S23}$$

$$\lim_{w_{\delta} \to 1} S_{k>0}^{*}(n) = \left[1 - 2^{(2-n)}\right](n-2)\ln(2),$$
(S24)

which are the functions one would derive if only the combinatorics of the problem were considered. The combinatorics essential define the shape of the entropy curves however, inclusion of an explicit kink energy penalty facilitates the fine-tuning required to allow a comparison with simulated data. At the opposite end of the scale, in the limit of $\delta U^* \to \infty$ kink formation is prohibited, and the Boltzmann weight of the kink penalty becomes $w_{\delta} = e^{-\beta^* \delta U^*} \to 0$. As a result, the straight chain is the only energetically viable configuration. Chains have only one accessible microstate, thus $\lim_{w_{\delta}\to 0} S_0^*(n) =$ 0. The entropy of the kinked chains state is somewhat undefined in this context, but mathematically also reduces to $\lim_{w_{\delta}\to 0} S_{k>0}^*(n) = 0$.

6.4 Free Energy

We will conclude this discussion with a look at the free energy distribution in the system. The total cluster free energy can be calculated using the familiar bridge equation linking the partition function to this macroscopic property,

$$\beta^* F^*(n) = -\ln Z(n),$$

= $-\ln \left[w_0 (1 + w_\delta)^{(n-2)} \right]$
= $(2 - n) \ln (1 + w_\delta) - \ln w_0.$ (S25)

In a similar manner, we can extract the internal energy from the partition function accordingly,

$$\beta^* U^*(n) = \beta^* \frac{\partial \beta^* F^*(n)}{\partial \beta^*} = -\ln w_0 + (2-n) \frac{w_\delta \ln w_\delta}{(1+w_\delta)}.$$
 (S26)

We can immediately identify and separate the energetic contributions,

$$\beta^* U_0^*(n) = -\ln w_0; \qquad \beta^* U_{k>0}^*(n) = (2-n) \frac{w_\delta \ln w_\delta}{(1+w_\delta)}, \tag{S27}$$

corresponding to straight chains and an excess due to kinking respectively. At this point we have all the pieces to perform a decomposition of the free energy into these two portions,

$$\beta^* F^*(n) = \beta^* F_0^*(n) + \beta^* F_{k>0}^*(n), \qquad (S28)$$

$$\beta^* F_0^*(n) = \beta^* U_0^*(n) - S_0^*(n), \tag{S29}$$

$$\beta^* F_{k>0}^*(n) = \beta^* U_{k>0}^*(n) - S_{k>0}^*(n).$$
(S30)

All that remains to be done is substitute the internal energy and entropy expression, which yields the following expressions,

$$\beta^* F_0^*(n) = -\ln w_0 - (1 + w_\delta)^{(2-n)} (n-2) \ln (1 + w_\delta), \tag{S31}$$

$$\beta^* F_{k>0}^*(n) = (1+w_\delta)^{(2-n)}(n-2)\ln(1+w_\delta) + (2-n)\ln(1+w_\delta).$$
(S32)

Movie captions

Supporting movie 1

This movie shows small angle X-ray scattering patterns taken at different rotation angles ω . At $\omega = 47^{\circ}$ peaks are enhanced by the form factor and are observed up to the 5th order in the horizontal and vertical directions and up to the 10th order in all diagonal directions.

Supporting movie 2

This movie shows typical dipolar structures formed by hematite cubes with shape parameter m = 4 and edge length $L \approx 1135$ nm coated with a 100 nm thick layer of silica shell in zero field environment. The effect of the particle shape on the dipolar structures is particularly evident in the dynamic behavior of the ten particle ring in the center of the field of view, which steadily fluctuates between a circular and rectangular loop.

Supporting movie 3

Simulation movie for a quasi-two-dimensional hematite cube (m = 4.0) system comprised of 256 particles with a surface density of 0.05 and magnetic coupling parameter of 10. The trajectory shown is at zero-field and runs for a length of 2.5×10^5 time-steps. We have duplicated the simulation box in order to clearly visualize the dipole orientations in the left-hand replica.