Supplementary Information: Spontaneous in-flight assembly of magnetic particles into macroscopic chains

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Synthesis procedure

Assembled iron nanocube chains are prepared in a gas phase cluster gun. The cluster source is quenching a hot iron vapor, steaming from magnetron head on the left side of Fig. S1, in a flowing stream of cool inert gas (argon) in aggregation chamber. The iron atoms condense and crystallize during gradual cooling process, producing NPs with a low internal temperature. The NPs are then extracted into a high vacuum region through a slit nozzle at the end of an aggregation chamber. The distance from the magnetron sputtering head to the slit is the principal variable controlling NPs size. Another variable is the sputtering power that determines the rate at which NPs are produced. The inert gas and vapor mixture undergo supersonic expansion into a region maintained at a pressure below 10^3 Torr. The ionized beam leaves the aggregation chamber passes through a slit 3 mm to the high vacuum region deferentially pumped with a flux of Ar of 80 cm³/min.

The growth of the nanostructures by cluster gun technique depends on various parameters, such as Ar gas flow, cluster gun power, NPs traveling distance, etc. In present work, the size evolution of the core/shell iron/iron oxide NPs is studied at constant Ar flow. The first row in Fig. S2 shows the NP evolution with the growth distance. It is observed that a minimum distance of d > 4 cm is needed to collect NPs (see very scarce number of NPs for d = 4 cm). In addition, for short growth distance (d < 7 cm) the size variation is very fast, while at large distance (d > 7 cm) no significant evolution is observed. At 5 cm travel distance average particle size is about 8 nm and at 8 cm distance an increase in particle size to 15 nm at the expense of the number of the generated particles was attained. The particles produced at 8 cm are dominantly of core/shell type. Further increase of the travel distance results in a small increase in the particle size: for 11 cm average size is 16 nm and for 13 cm average size is 17 nm. The lower row in Fig. S2 summarizes the evolution of the NP size with the gun power at fixed travel distance of 7 cm. In this case the size evolution is modest but the amount of NPs increase very fast. This work has been done without the use of a mass quadrupole that allows selecting the particle size.

Model

Magnetic NPs can have complex coupling involving both dipolar and exchange interactions. The atomic exchange interaction is relevant up to a length scale of 10nm.¹ Thus, dipolar



Figure S1: Scheme of the cluster gun, showing aggregation chamber, slit, and deposition chamber with differential pump exit.



Figure S2: Field emission SEM images $(500 \times x500 \text{ nm}^2)$ of core/shell iron NPs at constant Ar gas flow (80 cm³/min) and cluster gun power (20 W) as a function of NPs traveling distance (upper row). Lower row, SEM images of the obtained core/shell iron NPs as a function of cluster gun power at fixed (80 cm³/min) Ar gas flow and fixed traveling distance (7cm).



Figure S3: TEM images for NPs grown at different travel distance in the aggregation chamber (a) shell only particle are obtained for travel distance 5 cm and (b) core/shell particle for travel distances 11 cm.

coupling dominates in the formation of the structures on the length scales $10nm-100\mu m$, with many potential applications.²⁻⁶ Due to shape anisotropy, small single domain magnets behave like uniaxial magnets. We characterize the system using dipole-dipole interaction potential: it is assumed that each particle carries identical dipolar (magnetic) moment with magnitude $M_0 = m_s d^3$ where m_s is the magnetization and d the size of the cube. In this work two magnetic easy axes are possible: the one governed by the magnetite shell lying in the [111], and the one induced by the iron core oriented along the [100] direction. The analytic expressions for the magnetic field, of a sphere or an infinite cylinder, are part of all classical magneto-static textbook. For complex geometries we need to employ numerical solvers. Still, solution for bar magnet, deduced from the Maxwell equations can be also obtained analytically. For a magnetic bar magnetized along the y-axis, i.e., $[010]^7$ one finds:

$$B_x^{[010]}(x,y,z) = \frac{\mu_0}{4\pi} M_0 \sum_{k,l,m=1}^2 \log[z + (-1)^m z_{\rm b} + A_{\rm sq}^{klm}]$$
(1)

$$B_{y}^{[010]}(x,y,z) = -\frac{\mu_{0}}{4\pi} M_{0} \sum_{k,l,m=1}^{2} \frac{[y+(-1)^{l}y_{\rm b}][x+(-1)^{k}x_{\rm b}]}{|y+(-1)^{l}y_{\rm b}||x+(-1)^{k}x_{\rm b}|} \arctan\{\frac{|x+(-1)^{k}x_{\rm b}|[z+(-1)^{m}z_{\rm b}]}{|y+(-1)^{l}y_{\rm b}|A_{\rm sq}^{klm}}\}$$
(2)

$$B_z^{[010]}(x, y, z) = \frac{\mu_0}{4\pi} M_0 \sum_{k,l,m=1}^2 \log[x + (-1)^k x_{\rm b} + A_{\rm sq}^{klm}]$$
(3)

where $A_{\rm sq}^{klm} = \sqrt{[x + (-1)^k x_{\rm b}]^2 + [y + (-1)^l y_{\rm b}]^2 + [z + (-1)^m z_{\rm b}]^2}.$

For a bar magnetized along the x-axis, it is sufficient to rotate the system in following

way: $B_x^{[100]}(x, y, z) = B_z^{[010]}(-y, x, z), B_y^{[100]}(x, y, z) = -B_x^{[010]}(-y, x, z), \text{ and } B_z^{[100]}(x, y, z) = B_y^{[010]}(-y, x, z), \text{ and for a bar magnetized along the } z-\text{axis}, B_x^{[001]}(x, y, z) = B_x^{[010]}(x, z, -y), B_y^{[001]}(x, y, z) = -B_z^{[010]}(x, z, -y), B_z^{[001]}(x, y, z) = B_y^{[010]}(x, z, -y).$ Finally, for a magnetic field of a cube $(x_b = y_b = z_b)$ magnetized along principal diagonal (i.e., [111]), magnetic field is the sum of the previous expressions, $\vec{B}^{[111]} = (\vec{B}^{[100]} + \vec{B}^{[010]} + \vec{B}^{[001]})/\sqrt{3}$. A significant uncertainty margin regarding magnetic moment of the magnetic particles exist. The hematite has small $(m_s \approx 2.2kAm^{-1})$, while magnetize and iron have a large spontaneous magnetization, i.e., $m_s \approx 480kAm^{-1}$ and $1600kAm^{-1}$, respectively.⁸

In case of pure iron particles, the reference magnetic interaction energy $\epsilon = \mu_0 M_0^2 / 4\pi d^3$, i.e., was estimated to be in the order of 25 eV, i.e., $10^3 k_B T$, where T = 300K is the temperature and k_B is the Boltzmann's constant. The magnetic interaction energy ϵ decreases with increase of the iron oxide shell thickness, see Fig. S4. The magnetic field generated by one particle at the c.m. of the other particle (placed side by side) is $B_0 = \mu_0 M_0 / (2\pi d^3) = 160$ mT.



Figure S4: Dependence of reference magnetic interaction energy $\epsilon = \mu_0 M_0^2 / 4\pi d^3$ with thickness of magnetite shell d_{shell} for d = 25 nm core/shell iron/iron oxide cube. Inset shows ratio of shell to total volume of the cube.

The previous formula is applicable for the analytical analysis of dipolar interaction of



Figure S5: (a) Uniformly [001] magnetized magnetic cube, (b) nine dipole model for [001] magnetized cube, (c) uniformly [111] magnetized magnetic cube, (d) nine dipole model for [111] magnetized cube, and (e) mechanical contact model representation of the cube. Top (upper row) and side (lower row) view are given for comparison.

cubes but it is not practical for running a molecular dynamics simulations. We construct a model which combines numerical precision with computational efficiency.

The cubes are modeled as cluster of hard spheres filling a cubical frame. A magnetic cube with side d is represented with nine spheres a big sphere in the center with radius d/2 and eight smaller spheres touching the inner corners of the cube and the big central sphere with radii $(2 - \sqrt{3})d/2$. A cube is therefore represented using a potential energy of interaction $U(\vec{r}_{ij})$ between pairs of the point-like dipoles with the sphere centers located at \vec{r}_i and \vec{r}_j can be written as:

$$U_{\rm m}(\vec{r}_{ij}) = \frac{\mu_0}{4\pi} \left[\frac{\vec{m}_i \cdot \vec{m}_j}{r_{ij}^3} - 3 \frac{(\vec{m}_i \cdot \vec{r}_{ij})(\vec{m}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \right],\tag{4}$$

where $r_{ij} = |\vec{r}_{ij}| = |\vec{r}_j - \vec{r}_i|$, and $i, j = 1 \cdot 9$. The magnetic moments in this model carry a fraction of the of total magnetic moment. The magnetic moment m_i is expressed as $m_i = I^s v_i$, where v_i is the volume of the magnetic part of the particle. The volume of the central particle is $v_1 = \pi/6$ and the one of the smaller particles located at the corners is $v_{2...9} = \pi (2 - \sqrt{3})^3/6$. The magnetic density which insures same energy between uniformly magnetized cube placed on top of each other (minimal energy configuration) as in case of uniformly magnetized cubes is $I^s \approx 2.1 \cdot M_0/d^3$. This magnetic density is the same for both investigated magnetization directions, i.e., [001] and [111].

Using nine dipoles, we take into account the interaction of the cube corners which was not taken into account in previously used models, Ref.⁹ The principle change is in the position of the second maximum when one c.m. of one particle is on the corner of the other, see Fig. S6. While in single dipole model⁹ the secondary (i.e., head-tail minimum) lies at $\Delta_{xy}^1/\sqrt{2}d \approx 0.39$, in our nine dipole model is at $\Delta_{xy}^9/\sqrt{2}d \approx 0.45$ significantly closer to the result for a uniformly magnetized cube $\Delta_{xy}^{unif}/\sqrt{2}d = 1/2$. The position of the secondary peak is important since it contributes to the flexible movement of the chain, i.e., particle at the corner can easily flip over the side to a similar energy state. Thereby, the total potential energy of magnetic interaction of two particles with indices α, β in a given structure $U_{\rm m}^{\rm tot}$ is given by a sum over pairs of dipoles :

$$U_{\rm m}^{\alpha\beta} = \sum_{\substack{i,j=1..9\\i>j}} U_{\rm m}(\vec{r}_{ij}^{\alpha\beta}).$$
(5)

The contact potential of the cubes is represented by four overlapping spheres per edge with diameter radii $(2 - \sqrt{3})d/2$, having a total of 32 spheres, and the central sphere with radius d/2. These, in fact, cuboids are rigid bodies with fixed distances between spheres. This model is mainly chosen to account for cube overlaps while at the same time creating a smooth and incommensurate surfaces allowing smooth gliding of one cube over the other. The incommensurability is important since it prevents the system to mechanically lock in commensurable states and enables smooth gliding of one cube over the other. We describe the effect of isotropic contact interaction between the spherical particles using a minimal model, i.e., representing them by the soft-core beads. The spheres therefore interact isotropically by means of truncated at minima $r_{\rm cut} = 2^{1/6}\sigma$ and shifted Lennard-Jones potential, also known as Weeks-Chandler-Andersen (WCA) potential. The interaction is defined as: $U_{\rm LJ}^{\rm cut}(r) =$ $U_{\rm LJ}(r) - U_{\rm LJ}(r_{\rm cut}), r < r_{\rm cut}$ and $U_{\rm cut} = 0, r \ge r_{\rm cut}$, where $r_{\rm cut}$ is the distance at which the potential is truncated, and $U_{\rm LJ}(r)$ is the conventional Lennard-Jones (LJ) potential, i.e.,



Figure S6: Comparison of the interaction energy of two uniformly magnetized cubes considering a nine dipole and a single dipole models.⁹ The minimal energy for different positions along the diagonal of the cube are shown.

 $U_{\rm LJ}(r) = -4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. The parameter ϵ corresponds to the energy scale of the interaction and σ is related to the characteristic diameter of the spheres δ . i.e., $\sigma = \delta/2^{1/6}$ and $\delta/d = 1$ and $(2 - \sqrt{3})d$ for large and small spheres respectively. The value of the sphere repulsive contact potential is taken $\epsilon_r = 7 \cdot 10^{-16}$ J for particles with the same d = 25nm size of the cube (i.e., $\epsilon_r = 800 U_{\rm m}^{\alpha\beta}$).

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