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Crystallization by particle attachment is a colloidal assembly process

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The nucleation of crystals has long been thought to occur through the stochastic association of ions, atoms or molecules to form critical nuclei, which will later grow out to crystals¹. Only in the past decade has the awareness grown that crystallization can also proceed through the assembly of different types of building blocks^{2,3}, including amorphous precursors⁴, primary particles⁵, prenucleation species^{6,7}, dense liquid droplets^{8,9} or nanocrystals¹⁰. However, the forces that control these alternative pathways are still poorly understood. Here, we investigate the crystallization of magnetite (Fe₃O₄) through the formation and aggregation of primary particles and show that both the thermodynamics and the kinetics of the process can be described in terms of colloidal assembly. This model allows predicting the average crystal size at a given initial Fe concentration, thereby opening the way to the design of crystals with predefined sizes and properties.

Magnetite (Fe₃O₄) is a naturally occurring ferrimagnetic iron oxide¹¹ with great biological^{12,13} and geological¹⁴ importance that has a large variety of technological and biomedical applications¹⁵. The magnetic properties of Fe₃O₄ depend on the size and shape of the crystals¹⁶. Therefore, predicting the size and shape of magnetite crystals is important for the rational synthesis of crystalline materials with predetermined properties tuned to specific applications.

We synthesized Fe₃O₄ using the partial oxidation of ferrous hydroxide (Fe(OH)₂) (see Methods and Supplementary Information¹⁷). In a titration set-up, the pH of a Fe²⁺ solution was increased from 3–4 to 9 (Supplementary Fig. 1), leading to the precipitation of the Fe(OH)₂ precursor, which appeared as ultra-thin (~1 nm) platelets (Fig. 1a) under cryogenic transmission electron microscopy (cryo-TEM). Subsequent titration of the oxidant (KNO₃) led to conversion of the precursor into magnetite crystals (Fig. 1c–f). During this process, particles, ~2 nm in diameter, formed in solution (Fig. 1b). Electron diffraction analysis (see Methods, Supplementary Fig. 2 and Supplementary Discussion 1) of the primary particles (PPs) showed two weak reflections with *d* spacing of 1.96 Å and 1.55 Å, respectively (Fig. 2a and Supplementary Fig. 3). These reflections show that the PPs represent a crystalline precursor phase and are not loose hydrated clusters¹⁸. It is difficult to unequivocally identify this mineral phase based on only two reflections, as iron oxides and hydroxides often present similar reflections¹¹. In fact, a ~1.5 Å *d* spacing is found in many iron oxides and hydroxides, including magnetite (440), green rust (113) and ferrihydrite

(115)^{11,19}. The presence of such a reflection corroborates that the electron diffraction signal is due to the presence of an ordered iron (oxy-)hydroxide phase rather than an environmental impurity. The 1.96 Å PP *d* spacing is not consistent with magnetite nor green rust (Supplementary Table 2) but it is close to the spacing of (113) planes of ferrihydrite, a known magnetite precursor phase^{5,20}. As two-line ferrihydrite exhibits only two diffraction peaks²¹, we speculate that the PP crystalline phase may be structurally similar, but contain both Fe²⁺ and Fe³⁺ ions, rather than only Fe³⁺ ions as is the case for two-line ferrihydrite.

At later stages, nanogranular particles (Fig. 1c–e) diffracting as magnetite (Fig. 2a and Supplementary Fig. 2i,j) were observed. The formation of crystals with granular morphology is not compatible with a dissolution–reprecipitation process like Ostwald ripening. Hence, magnetite must have formed through colloidal assembly of the PPs, as also reported for the co-precipitation of Fe²⁺ and Fe³⁺ (ref. 5). The PPs converted into magnetite after aggregation, as shown by electron diffraction analysis of the granular magnetite crystals (Fig. 2a and Supplementary Fig. 2i,j).

With continued addition of the oxidant, the nanogranular crystals grew in size and number (with the constituting PPs still being recognized; Fig. 1e), at the expense of the precursor crystals, which developed cracks and subsequently dissolved (Supplementary Fig. 4c). The final product consisted of faceted magnetite crystals (Fig. 1f), indicating that, in addition to the crystallization via particle attachment (CPA)², coarsening occurs, minimizing the total energy of the developing crystals.

Depending on the initial Fe concentration ([Fe]₀), which ranged from 0.5 to 100 mM, the magnetite nanocrystals had an average radius ($R_{\text{xtl}}^{\text{exp}}$) between 5 and 96 nm with a coefficient of variation of 26–41% (Fig. 2b, Supplementary Fig. 5 and Supplementary Table 1).

Vibrating sample magnetometry (see Methods and Supplementary Fig. 6) produced values for coercivity, remanent magnetization and saturation magnetization that are in good agreement with literature data for pure magnetite²². Surprisingly, the average crystal size increased with increasing [Fe]₀ (Fig. 2b), in contrast to conventional crystallization experiments where the reverse is observed^{23,24}.

Although it has been shown previously that the involvement of PPs lowers the total Gibbs free energy of crystallization (ΔG_{xtl}) compared to classical theory^{5,6}, the role of the chemical transformation of the PP that takes place in this process has not yet been discussed.

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Fig. 1 | Cryo-TEM of different stages of magnetite formation. **a**, Solution at pH $\approx$ 7.5 before the addition of NO_3^- . **b**, Primary particles formed after the addition of NO_3^- on a graphene oxide support (see Supplementary Materials and Methods for details). **c,d**, Reaction product after the addition of 35% (**c**) and 40% (**d**) of the total stoichiometric amount of NO_3^- . **e**, Enlargement of a growing nanogranular magnetite crystal. **f**, Magnetite crystals in the end product.

We now consider ΔG_{xil} via aggregation of PPs to have three different components associated with (1) formation of x PPs composed of an intermediate phase (ΔG_{pp}), (2) aggregation of the PPs into clusters of x PPs (ΔG_{clust}) and (3) conversion of the clusters into the final crystalline phase (ΔG_{conv}):

$$\Delta G_{\text{xil}} = x\Delta G_{\text{pp}} + \Delta G_{\text{clust}} + \Delta G_{\text{conv}} \quad (1)$$

Considering the PPs as a crystalline condensed phase (Fig. 2a and Supplementary Fig. 3), rather than loose hydrated clusters¹⁸, we can write equation (1) as a function of a bulk and surface term:

$$\Delta G_{\text{xil}} = \frac{4}{3}\pi R_{\text{clust}}^3 (g_{\text{pp}} + \phi\Delta g_{\text{conv}}) + 4\pi R_{\text{clust}}^2 (\gamma_{\text{pp}} + \phi\Delta\gamma_{\text{conv}}) \quad (2)$$

where R_{clust} is the radius of a cluster composed of x PPs and $\Delta g_{\text{conv}} = (R_{\text{xil}}^3/R_{\text{clust}}^3)g_{\text{xil}} - g_{\text{pp}}$ represents the change in bulk energy density and particle volume for the conversion of clusters into the final crystals with size R_{xil} . $\Delta\gamma_{\text{conv}} = (R_{\text{xil}}^2/R_{\text{clust}}^2)\gamma_{\text{xil}} - \gamma_{\text{pp}}$ is the corresponding change in interfacial energy, and $0 < \phi < 1$ represents the degree to which the cluster has converted to the crystal (see Supplementary Materials and Methods).

Here, ΔG_{xil} does not depend on the size of the PPs. If no intermediate phase is involved ($g_{\text{pp}} = g_{\text{xil}}$, $\gamma_{\text{pp}} = \gamma_{\text{xil}}$) or if the intermediate phase converts instantaneously into the final crystalline phase

($\phi = 1$), our model recovers the classic expression for the free energy of crystallization (Fig. 3a). In the limit of $\phi = 0$, equation (2) reduces to the expression proposed in ref. ⁵ (see Supplementary Materials and Methods).

In agreement with the literature²⁵, the model further predicts that the conversion of the intermediate phase becomes favourable above a critical cluster size, R_{conv} , which depends on the change of interfacial and bulk energy upon conversion:

$$R_{\text{conv}} = -\frac{3\Delta\gamma_{\text{conv}}}{\Delta g_{\text{conv}}} \quad (3)$$

Hence, in the early stages ($R_{\text{clust}} < R_{\text{conv}}$) the crystallization process will be dominated by PP clustering, with the conversion to magnetite occurring at a later stage (Fig. 3a,b).

The crystallization, especially the final crystal size, therefore strongly depends on the kinetics of PP formation and clustering. The role of Coulombic interactions in regulating the kinetics of crystallization processes involving PPs has been recognized by several authors^{6,26,27}.

Charged colloidal particles in water are surrounded by an electric double layer²⁸. When the particles approach, the overlap of these double layers creates a repulsive interaction that disfavors clustering. However, at close distances the attractive forces dominate and the colloids aggregate irreversibly, as

Fig. 2 | Quantitative analysis of the TEM images. a, Radially averaged electron diffraction patterns at different stages of magnetite formation. As a comparison, data are also shown for the dry (grey curve) and wet (red curve) graphene oxide support used for the analysis of the PPs (blue curve) and platelets (green curve). Quantifoil carbon film was used for magnetite (black curve). **b,** Average crystal radius, $R_{\text{xtl}}^{\text{exp}}$, determined by TEM data as a function of $[\text{Fe}]_i$. Average crystal radii were obtained by measuring 100 to 400 individual crystals per sample. The dashed line is a guide to the eye. Error bars represent standard deviation in the mean.

described by Derjaguin–Landau–Verwey–Overbeek (DLVO) theory^{29,30}. This balance between long-range repulsion and short-range attraction that results in a barrier (ΔE_{int}) affecting the kinetics of PP aggregation has not yet been considered in crystallization theories.

Our kinetic model assumes the cluster-to-crystal conversion to occur only at a late stage of the process, and describes the changes in the number of PPs (N_{pp}) and clusters (N_{clust}) via four kinetic constants, k_0 , $k_{\text{p,p}}$, $k_{\text{c,c}}$ and $k_{\text{p,c}}$ (see Figs. 3f and 4a and Supplementary Materials and Methods for details). Constant k_0 describes the formation of the PPs, modelled with zero-order kinetics, because the supersaturation level of the Fe in solution is constant and determined by the solubility product of the precursor; $k_{\text{p,p}}$ describes the aggregation of two PPs, and can be regarded as the initiation step; $k_{\text{p,c}}$ and $k_{\text{c,c}}$ describe two possible growth mechanisms, via the addition of a single PP to a cluster or via the aggregation of two clusters, respectively (Fig. 4a). Constants $k_{\text{p,p}}$, $k_{\text{p,c}}$ and $k_{\text{c,c}}$ depend on the repulsive barriers of the interaction potential between the particles ($\Delta E_{\text{int}}^{\text{p,p}}$, $\Delta E_{\text{int}}^{\text{p,c}}$, $\Delta E_{\text{int}}^{\text{c,c}}$, respectively) and were estimated using DLVO theory^{29,30} and literature data (Supplementary Discussion 2), for the different experimental conditions (pH, total ion concentration $[\text{I}]$). The value of k_0 cannot be directly measured nor predicted theoretically. Hence, k_0 is used as a fitting parameter in the model (Supplementary Discussions 2 and 4).

The clusters are modelled with an effective average size $\bar{R}_{\text{clust}}$ (see Supplementary Materials and Methods and Supplementary Discussion 4). Under this approximation, the evolution of N_{pp} and N_{clust} follows from

$$\frac{dN_{\text{pp}}}{dt} \approx k_0 - 2k_{\text{p,p}}N_{\text{pp}}^2 - k_{\text{p,c}}N_{\text{pp}}N_{\text{clust}} \quad (4)$$

$$\frac{dN_{\text{clust}}}{dt} \approx k_{\text{p,p}}N_{\text{pp}}^2 - k_{\text{c,c}}N_{\text{clust}}^2 \quad (5)$$

Numerical solution of equations (4) and (5) using $N_{\text{pp}}(t=0)=0$ and $N_{\text{clust}}(t=0)=0$ as starting conditions yields the evolution of N_{pp} and N_{clust} over time (Fig. 4b,c). The model predicts that the clustering process initially dominates, with N_{clust} increasing until the reaction reaches the steady state (Fig. 4b,c). At the steady state, N_{pp} and N_{clust} remain constant over time and hence $dN_{\text{pp}}/dt=0$ and $dN_{\text{clust}}/dt=0$ (Fig. 4b). With these conditions an analytical solution for the steady-state value of N_{clust} ($N_{\text{clust}}^{\text{ss}}$) can be derived by solving equations (4) and (5):

$$N_{\text{clust}}^{\text{ss}} = \sqrt{\frac{k_0}{2k_{\text{c,c}} + \sqrt{\frac{k_{\text{c,c}}}{k_{\text{p,p}}}}}} \quad (6)$$

Equation (6) can be used to readily predict the number of crystals formed in solution (N_{xtl}), when the reaction reaches the steady state ($N_{\text{xtl}}^{\text{ss}} = N_{\text{clust}}^{\text{ss}}$). From this, the expected average value of the crystal radius, $R_{\text{xtl}}^{\text{ss}}$, can be estimated using the principle of conservation of mass (Supplementary Discussion 3 and Supplementary equation (27)). Similarly, we can estimate the experimental number of particles formed in solution ($N_{\text{xtl}}^{\text{exp}}$) from the experimental average radius of the crystals ($R_{\text{xtl}}^{\text{exp}}$).

The values of $N_{\text{xtl}}^{\text{ss}}$ (Fig. 4d) and $R_{\text{xtl}}^{\text{ss}}$ (Fig. 4e), predicted using equation (6) and Supplementary equation (27), match with the experimental data independent of the value chosen for the effective average cluster size, $\bar{R}_{\text{clust}}$. Under the experimental conditions used, our model predicts the interaction potentials to be barrierless for the regime $[\text{Fe}]_i \gtrsim 5$ mM, while at $[\text{Fe}]_i \lesssim 5$ mM a barrier appears that increases with decreasing $[\text{Fe}]_i$ (Fig. 3c–e). This is due to the associated differences in $[\text{I}]$, and in particular in the concentrations of counterions (Cl^- , K^+) and added oxidant. Consequently, the model predicts a decrease of $N_{\text{xtl}}^{\text{ss}}$ with increasing $[\text{Fe}]_i$ until $[\text{Fe}]_i \approx 5$ mM, and a constant value of $N_{\text{xtl}}^{\text{ss}}$ for $[\text{Fe}]_i \gtrsim 5$ mM (Fig. 4d). These predictions perfectly match the change in $N_{\text{xtl}}^{\text{exp}}$, as derived from the experimentally observed crystal radii $R_{\text{xtl}}^{\text{exp}}$. Concomitantly, the predicted crystal radii $R_{\text{xtl}}^{\text{ss}}$ follow the experimental ones over the entire $[\text{Fe}]_i$ interval (Fig. 4e).

The rate constants for the cluster–primary particle aggregation $k_{\text{p,c}}$ and cluster–cluster aggregation $k_{\text{c,c}}$ vary with $[\text{I}]$ (Fig. 3f). At low $[\text{I}]$, $k_{\text{p,c}} \gg k_{\text{c,c}}$ and crystals are predicted to grow at comparable rates and to have narrow size distributions. However, as $[\text{I}]$ increases, $k_{\text{c,c}}$ increases relative to $k_{\text{p,c}}$ and their values become comparable. Cluster aggregation will lead to a decrease in N_{clust} and hence to a decrease in N_{xtl} and a concomitant increase in R_{xtl} with growth occurring in steps of unequal size, resulting in more polydisperse crystals. Indeed, when magnetite was synthesized at high $[\text{I}]$, using $[\text{Fe}]_i = 0.9$ mM and 8 mM of KCl, the average size of the crystals ($R_{\text{xtl}}^{\text{exp}} = 78 \pm 30$ nm, $N_{\text{xtl}}^{\text{exp}} = 1.3 \times 10^{12}$) was significantly higher than those grown in the absence of added salt ($R_{\text{xtl}}^{\text{exp}} = 19 \pm 5$ nm, $N_{\text{xtl}}^{\text{exp}} = 9.2 \times 10^{13}$) with a corresponding increase in the coefficient of variation from 26% to 38% (Supplementary Fig. 7).

Hence, we demonstrate that for this CPA system the so-called non-classical crystallization mechanism can be fully explained by classical concepts of colloidal theory. We show that the primary

Fig. 3 | Thermodynamic model. **a**, Comparison between the ΔG_{xtl} curves as a function of R_{clust} for $\phi = 1$ (green curve), $\phi = 0.5$ (blue curve) and $\phi = 0$ (red curve) and $R_{\text{xtl}} = R_{\text{clust}}$ (no size variation upon conversion). The plus symbols represent classical nucleation and the thick black dots indicate the most favourable thermodynamic pathway. The vertical red dashed line indicates R_{conv} . **b**, Contour plot showing ΔG_{xtl} as a function of ϕ and R_{clust} . The vertical dashed line indicates R_{conv} while the white arrow indicates our proposed crystallization pathway. Data are generated using $\Delta g_{\text{pp}} = -1 \times 10^6 \text{ kJ m}^{-3}$, $\Delta g_{\text{xtl}} = -2 \times 10^6 \text{ kJ m}^{-3}$, $\gamma_{\text{pp}} = 0.2 \text{ J m}^{-2}$ and $\gamma_{\text{xtl}} = 1 \text{ J m}^{-2}$ as estimates for the generic bulk (on the order of a few hundreds of kJ mol^{-1}) and surface energy densities of inorganic materials²⁸. **c–e**, Pair interaction potential $V(H, t)$ as a function of the interparticle distance H at the beginning of the crystallization process ($t = 0$) between two primary particles (**c**), a primary particle and a cluster (**d**) and two clusters (**e**), calculated using Supplementary equation (23) (Supplementary Discussion 2), showing all interaction potentials are barrierless for $[\text{Fe}]_t > 5 \text{ mM}$, while at $[\text{Fe}]_t < 5 \text{ mM}$ a barrier appears and increases with decreasing $[\text{Fe}]_t$. The insets in **c–e** show the short-range primary minima of $V(H, t)$. **f**, Kinetic constants as a function of the total ion concentration using Supplementary equations (22) and (23) (Supplementary Discussion 2).

particles involved in the process behave as colloids, and that the kinetics of the crystallization process is regulated by the interaction potential between the particles and by the rate of transformation of the precursor particles. This generic model allows us to predict the size and to qualitatively interpret variations in the polydispersity of the crystals due to changes of the solution conditions. The

model can be adapted to describe the specific case where crystals are formed via the oriented attachment of crystalline building blocks³¹ by accounting for the relative orientation of the colliding particles and introducing orientation-dependent interactions. However, in such a case, less complex polymerization models might be a more appropriate choice^{32,33}.

Fig. 4 | Model of the CPA process. **a**, Schematic of the formation (left), colloidal assembly (middle) and conversion of the PPs (right) into magnetite. **b**, Evolution of N_{pp} and N_{clust} over time according to numerically solved equations (4) and (5) at $[\text{Fe}]_i = 100 \text{ mM}$. **c**, Evolution of N_{clust} at different values of $[\text{Fe}]_i$. **d**, Comparison between the experimentally measured (N_{xtl}^{exp} , black markers) and theoretically predicted (N_{xtl}^{ss} , continuous curves) average number of crystals. **e**, Comparison between experimental (R_{xtl}^{exp} , black markers) and predicted (R_{xtl}^{ss} , continuous curves) values of the crystal radius. Average experimental crystal radii were obtained from TEM data by measuring 100 to 400 individual crystals per sample. The predicted N_{xtl}^{ss} and R_{xtl}^{ss} values were calculated using equation (6) and Supplementary equation (27), respectively. Different curves are obtained using different values for the effective average cluster size $\bar{R}_{clust}$, which resulted in different fitted k_0 values.

The realization that crystallization from primary particles is a colloidal assembly process will allow us to control such processes, for example through the use of external stimuli³⁴ or confinement³⁵. We expect the intersection of crystallization theory and colloidal theory to bring a new level of understanding to crystal formation mechanisms.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41563-019-0511-4>.

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Author contributions

N.A.J.M.S. and G.M. conceived and designed the experiments. G.M. performed the synthetic experiments. G.M., H.F. and P.H.H.B. conceived and designed the TEM and cryo-TEM experiments. G.M. and P.H.H.B. performed the TEM and cryo-TEM acquisition and analysis. A.I. developed the theoretical model. G.d.W. supervised the theoretical modelling. A.A. and T.Y. performed the vibrating sample magnetometry analysis. N.A.J.M.S., G.d.W., G.M. and A.I. contributed to writing the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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Methods

Synthesis of magnetite. Magnetite was synthesized by using the partial oxidation method. The reaction was carried out by using an automated titration system (Methrom Applikon) consisting of two 20 ml Dosino dosing units, a glass pH microelectrode and a magnetic stirring plate, all connected to two 905 Titrand titration units controlled by the TIAMO 2.3 software. All the syntheses were performed at room temperature and with 25 ml total volume inside a 50 ml double-walled glass vessel under a constant flow of room-temperature argon. The overall synthetic set-up was located inside a glovebag filled with nitrogen gas in which the oxygen percentage was kept below 5% and constantly measured by a sensor. All the solutions were prepared with Milli-Q water and degassed with N_2 for at least 30 min before use. KOH and KNO_3 were purchased from Merck, while $FeCl_2 \cdot 4H_2O$ was purchased from Sigma-Aldrich, and used as received. The pH of solution containing Fe^{2+} was gradually increased by adding KOH up to a pH of 9, which resulted in the formation of a ferrous hydroxide precursor phase, $Fe(OH)_2$. The pH was held constant during addition of the oxidant KNO_3 in a stoichiometric ratio of 3:5 $Fe:NO_3^-$, which oxidized the precursor to magnetite. Additional discussion and details are provided in the Supplementary Material and Methods.

TEM. For conventional dry TEM, we used 200 mesh Cu grids with continuous carbon films (Agar Scientific). The sample was prepared by applying 50 μ l of solution onto the TEM grid and drying by air. For cryo-TEM, we used 200 mesh Cu grids with Quantifoil R 2/2 holey carbon films (Quantifoil Micro Tools) and lacey carbon films (Electron Microscopy Science). We used an automated vitrification robot (FEI Vitrobot Mark III) to plunge each sample in liquid ethane in preparation for cryo-TEM³⁶. All TEM grids were surface plasma treated for 40 s using a Cressington 208 carbon coater before use. Conventional dry samples were analysed on an FEI Technai 20 system (type Sphera) operated at 200 kV, equipped with a LaB6 filament and a 1 k $\times$ 1 k Gatan charge-coupled device (CCD) camera. Cryogenic samples were analysed on a TU/e cryoTITAN system (FEI, www.cryotem.nl) operated at 300 kV, equipped with a field emission gun, a postcolumn Gatan energy filter (GIF) and a post-GIF 2 k $\times$ 2 k Gatan CCD camera. Gatan DigitalMicrograph (including DiffTools) and MATLAB were used for TEM image and selected area electron diffraction pattern analysis.

Cryo-TEM analysis of the primary particles. To characterize the chemical nature of the primary particles observed in cryo-TEM, we used graphene oxide-coated grids (GOx grid) to reduce significantly the thickness of the vitreous ice layer as compared to conventional carbon-coated grids³⁷. The GOx grids were prepared following the procedure reported in ref. ³⁷. This method allows us to decrease

the background contribution, enhancing the signal from the PPs in the electron diffraction patterns, and to increase the image contrast. Moreover, the graphene oxide can be used as an internal standard to evaluate the instrumental broadening line of the reflections and produce a more accurate interpretation of the signals. The obtained electron diffraction patterns are shown in Fig. 2a and Supplementary Fig. 2.

Crystal size measurements. Crystal size distributions were determined by manually measuring the long and short axes of more than 100 individual crystals per sample in TEM images using a MATLAB program. The average radius of a crystal was taken to be half of the sum of the long and short axes of the crystal. Crystal sizes are reported as mean $\pm$ standard deviation of the mean (Supplementary Table 1).

Vibrating sample magnetometry. Vibrating sample magnetometry measurements were performed on a TM-VSM101483N7-MRO magnetometer (Tamakawa Co.) with a 14 mm pole piece gap. Samples were prepared by dispersing between 10 and 1 mg dried magnetite in an aliquot of 50 ml 1% agarose solution. The mixture gellified in a few minutes and thus fixated the magnetite, allowing quantification of remanent magnetization and coercivity. The magnetic hysteresis loops were acquired at room temperature from +1 T to -1 T and back in a total of 116 steps (time constant 10 ms, total measurement time $\sim$ 30 min). The results were corrected for the diamagnetic background of the sample container/holder and normalized to the sample mass. Additional discussion and details are provided in the Supplementary Material and Methods.

Data availability

All data are available from the authors upon reasonable request.

Code availability

All Python and Mathematica scripts used for the theoretical modelling are available from the authors upon reasonable request.

References

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