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ELECTRONIC SUPPLEMENTARY INFORMATION

Extensive characterization of magnetic microrods observed by optical microscopy

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ESI, Figure. S1: General scheme of the experiments



Fig. S1 General scheme of the experiments. The four groups of experiments explicit what are the measurements realized on the same rod, or on the same bulk sample (hexagons). Some variables (red round circles) are directly deduced by some measurements (squared boxes) or from a combination of them.

ESI, Figure S2: Magnetization curves of the rod nanoparticles



Fig. S2 Magnetization curves of the nanoparticles used to prepare the rods. The magnetization curves M(H) were obtained by vibrating sample magnetometry on a 3.9% volume fraction ferrofluid suspension of non-aggregated citrated particles. At this low concentration, the magnetic interaction between the particles is negligible and thus, no demagnetizing field takes place. Data have been extrapolated as if the solution volume fraction were 100%. The main figure is a portion of the magnetization cycle (the full cycle is shown in the grey inset) for the low values of the field at which the flexural experiments were performed. Green: field is increased, Red: field is decreased (refer to the left-axis for the scale). The slight shift between the increasing and decreasing curves ascribes to a known thermal drift of the Hall probe gaussmeter used to measure the magnetic induction, and not for a remanent magnetization: the surperparamagnetism of such a suspension being well known ¹. Blue data: the magnetic susceptibility $\chi^v = \frac{M}{H}$ deduced from the magnetization values (scale on the right axis) varies considerably, in particular for a low induction field.

¹W. C. Elmore, The Magnetization of Ferromagnetic Colloids, *Phys. Rev.*, 1938, **54**(12), 1092–1095.

ESI, note 1: Optical and Atomic Force Microscopy measures of the rod radius

Much attention is necessary for the precise measurement of the radius r, on which depends the further determination of other parameters such as the Young modulus Y ($Y = \frac{4}{\Pi}r^{-4}C$ for cylindrical rods ²), the magnetic susceptibility $\chi \propto C r^{-2}$ (ESI[†], note 2), and hence the particle volume fraction $\phi \propto \chi$. We therefore searched for a precise direct determination of the radius of individual rods. Unfortunately, the typical diameter size (200-800 nm) was in the order of the Abbe's resolution limit $\rho = \frac{0.61\lambda}{NA} \sim 250$ nm (NA is the numerical aperture of the objective and λ the wave length). We thus developed a method to measure the rod radius inspired by the measurement of the length of sub-micron large bacteria by fluorescent microscopy 3 and driven by the assumption that in reflection microscopy, individual nanoparticles of the rod behave as individual point sources, like fluorescent particles in biological samples. We neglected the possible interference between them as ascribed from weak coherence of the light source. We also adopted the simple viewpoint where each diffuser reemits light with the same intensity. With the further hypothesis that at a given cross-section the nanoparticle concentration is homogeneous, the back scattered light intensity is simply dictated by the geometry and should be proportional to $2r_1\sqrt{1-(\frac{x}{r})^2}$, where x denotes for the abscissa along the orthogonal axis to the rod, r the radius in the transverse direction of the optical axis and r_1 the radius along the optical axis ($r_1 \neq r$ for an elliptic cross-section). In this view, the reflected light is therefore the point spread function of the microscope convoluted by the emitted light and should be: $I_r(x) = I_0(r) \int_{-r}^r J_1\left[a(s-x)^2\right] 2r_1\sqrt{1-(\frac{s}{r})^2} ds$ where J_1 is the Bessel function of the first kind and $a = \frac{2\pi NA}{\lambda}$. A common simplification consists in replacing J_1 by a Gaussian law with standard deviation $\sigma_{xy} = .21 \frac{\lambda}{NA}$.⁴ To test this model, we thus compared the expected intensity $I_r(x) = I_0 + I_1 \int_{-r}^r \exp\left[-\frac{(s-x-x_0)^2}{2\sigma_{xy^2}}\right] 2r\sqrt{1-(\frac{s}{r})^2} ds$ with many measures of grey intensity profiles from reflection images of the various rods (Fig. 1C and ESI^{\dagger}, S2). I_0, I_1, x_0 and r where adjustable parameters. In all cases, the theoretical curve fitted well the measured curves. We could thus automatize the procedure to probe the rod along its entire length (every two pixels=91 nm, ESI⁺, Fig. S3).

²L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, Pergamon press, Oxford, 2nd edn, 1970.

³B. Zhang and J. Enninga, Automated super-resolution detection of fluorescent rods in 2D. *Biomedical Imaging:* Nano to Macro, 2006. 3rd IEEE International Symposium on, 2006, pp.1–4.

⁴D. Thomann, D. R. Rines, P. K. Sorger and G. Danuser, Automatic fluorescent tag detection in 3D with superresolution: Application to the analysis of chromosome movement, J. Microsc., 2002, **208**(1), 49–64.

To check the accuracy of these optical measures, we compared them with measures obtained by an AFM scan performed on the same optically analyzed rod. The AFM used was a MFP-3D-BIO from Azylum Research, mounted on an inverted Olympus optical microscope. The AFM cantilevers were OMCL AC160TS R3 probes from Olympus with nominal stiffness of 26 N/m, nominal tip height of 14 μ m, and nominal tip radius of 7 nm. The resonance frequency was 271 kHz and the scan rate was 1 Hz. The imaging was performed in the soft tapping regime. The images were acquired with lateral sizes ranging from 5 to 20 μ m. To measure the radius by analysis of the optical images, we used the same equipment as for the rest of the experiments (camera, objective and beam splitter). To avoid the difficulties of AFM on water immersed samples, we partially allowed the sample to dry before the scan. It is clear that the procedure somewhat damaged the rods (as shown by images taken before, during and after rehydratation) but we found that a greater variability of the rod cross-section was actually more suitable than homogeneous rods to compare both radius measurement methods. After AFM analysis, the samples were gently rehydrated with a pipette, without moving the sample from the microscope stage. Images taken before and after the procedure showed that no observable modification occurred during the procedure. The AFM scans were done in tapping mode in the soft tapping regime from which we derived the height and radius of the rod profiles from the AFM scans (ESI[†], Fig. S3) taking into account the geometry of the tips. The height was found to be smaller than the width diameter, indicating that their lower surface may have flattened on the coverslip while drying. In all cases, we found that the variation of the height and the width were strongly correlated. The model for the optical analysis also holds for elliptic cross-section (or half-cut elliptic section) through the adjustment of the fit variable I_1 .

We performed this analysis respectively on 15 rods made from the 13 nm (and also 8 nm) average diameter nanoparticle fractions. The graphs of ESI[†], Fig. S3 show the strong similitude between the profiles from the two methods for three rods. However, we find that rather than being stochastic, the sign of the difference between the two curves is persistent over micron-long distances. Our interpretation is that, given the low number of particles (see Table 1 and Fig. 3), the AFM tip scans the polymer hairy shell whereas the optical method accounts for the presence of the inorganic nanoparticles. The AFM precision could thus be affected by the presence of sticky blobs of polymer or nanoparticles onto the tip, or the presence of a heterogeneous water layer around the rod. Despite these differences, we found that the mean difference (averaged over the rod length) between AFM and optical measures were respectively 1.5, 1.9 and 12 nm and that the standard deviation was ranging from 20 to 30 nm. This latter value of 30 nm also appeared to be the typical standard deviation of the optical radius measured along a water-immersed rod and was retained to be the uncertainty of our optical measurement.



Fig. S3 Comparison of rod radius measurement by AFM and optical reflection image analysis for three different rods. A_1 - A_3 grey intensity map of the height measured by AFM. For each panel, the inset shows the reflection optical image of the same rod after the sample has been rehydrated (bars=2 µm). B₁-B₃ each panel corresponds to the A images and shows the AFM-measured height (black line), the AFM-measured radius deduced from the width (blue line), the radius derived from the optical analysis (red line) and the absolute difference between the blue and red measures (green line). For each curve the sampling was every 2 camera pixels=93 nm.

ESI, note 2: Theory of the magnetoelastic experiments

In this section, we detail the theoretical model used to deduce the magnetic susceptibly χ from the magnetoelastic bending of a cantilevered rod submitted to a uniform external field $\vec{B}_0 = \mu_0 \vec{H}_0$ $(\mu_0 \text{ is the vacuum permeability})$. As described in the main text, we assume that the rod geometrical parameters - the radius r, the length L, and the deflection δ of the rod tip - as well as its bending modulus C are known from independent measurements. As shown on (Fig. 2A), we note \vec{H} the field inside the rod and \vec{M} its magnetization. The symbols \parallel and \perp applied to any vector $(\vec{M}, \vec{B}_0, \vec{H}...)$ denote respectively their longitudinal and orthogonal projections on the rod. In absence of remanent field (the rods are superparamagnetic), the bulk rod material is characterized by a magnetic susceptibility which is defined as $\chi(H) = \frac{M}{H}$. We assume the material to be homogeneous and isotropic. In the absence of magnetic dipolar interaction between the nanoparticles ⁵, we also have $\chi(H) = \frac{\phi}{\phi^v} \chi^v(H)$ where ϕ and ϕ^v are respectively the volume fractions of the particles in the rod and in the ferrofluid of the same nanoparticles on which the measurement of χ^v was performed by vibrating sample magnetometry (VSM).

We first consider a non-deformable paramagnetic rod of size L and radius r, submitted to \vec{B}_0 oriented at an angle $\alpha = \frac{\pi}{2} - \theta$ with respect to the rod main axis (Fig. 2A). When $L \gg r$, the rod may be approximated by an infinite cylinder. In our case in which the medium is uniform and isotropic, the demagnetizing factors of the main $(n_{\parallel} = 0)$ and transverse $(n_{\perp} = 1/2)$ axis are easily computed ⁶. Using $H_{\parallel(\perp)} = H_{0\parallel(\perp)} - n_{\parallel(\perp)}M_{\parallel(\perp)}$ and $M_{\parallel(\perp)} = \chi(H_{\parallel(\perp)})H_{\parallel(\perp)}$ from the above definition of the magnetic susceptibility, we deduce for each direction the effective susceptibilities defined as: $M_{\parallel(\perp)} = \chi_{\parallel(\perp)}H_{0\parallel(\perp)}$ and which are: $\chi_{\parallel} = \chi(H_{0\parallel})$ and $\chi_{\perp} = \frac{\chi(H_{\perp})}{1+\chi(H_{\perp})/2}$.

In these conditions, each section of the cylinder is submitted to a magnetic torque per unit volume $\vec{\Gamma}_m = \vec{M} \wedge \vec{B_0}$. The contributions from the \parallel and \perp components yield its algebraic amplitude:

$$\Gamma_m = \Gamma_{m\parallel} + \Gamma_{m\perp} = \Delta \chi \sin(2\alpha) \frac{\pi r^2 B_0^2}{2\mu_0} \tag{1}$$

⁵F. Gazeau, E. Dubois, J. C. Bacri, F. Boue, A. Cebers and R. Perzynski, Anisotropy of the structure factor of magnetic fluids under a field probed by small-angle neutron scattering, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys., 2002*, **65**(3), 1–15.

⁶This result is obtained from symmetry considerations and the constraint that the sum of all each-axis demagnetizing factors equals unity. See : Osborn, Demagnetizing factors of the General ellipsoid, *Phys. Rev.*, 1945, **11** and **12**, 351. For $L/r \sim 100$, as in the experiments, the infinite cylinder is an excellent approximation with a relative error of $\sim 7 \times 10^{-3}$ (see ref. 8).

where

$$\Delta \chi = \chi(H_{\parallel}) - \frac{\chi(H_{\perp})}{1 + \chi(H_{\perp})/2}$$
⁽²⁾

depends on both components of the internal magnetic field.

Secondly, we now assume that the cylinder is a Hookean deformable solid of Young modulus Yand bending modulus $C = \frac{\pi}{4}r^4Y$. According to classical elasticity equations ⁷, the restoring torque per unit length of a bent cylinder is $\Gamma_b = C \frac{d^2\theta}{dl^2}$. The local torque balance equation (which may be obtained through minimization of the energy functional even when χ depends on H^8) is therefore:

$$C\frac{d^{2}\theta(l)}{dl^{2}} + \pi r^{2}\frac{\Delta\chi B_{0}^{2}}{2\mu_{0}}\sin\left[2\theta(l)\right] = 0$$
(3)

where l designates the curvilinear abscissa along the rod and θ the angle with respect to the orthogonal direction to the field (see Fig. 2A). However, this equation relies on the supporting hypothesis of equation (1) which holds for a single straight rod, not for a deformed cylinder that changes direction (i.e. bends) relatively to the external field. It remains approximatively valid ⁹ if each section of the rod magnetically responds to the external field independently of what happens in the rest of the rod. We thus designate it as the "independent model". We recently introduced an alternative so-called "axial model" ¹⁰, in which we hypothesized that for large χ the magnetization is mostly longitudinal and also approximatively constant along the rod main axis. In the same paper, using the dipolar approximation, we discussed of the validity of each model and showed that the "independent model" is actually true when $\chi \leq 2$ because with this low susceptibility, the main contribution to the internal field \vec{H} in any direction is the external field rather than the magnetic self-induction of the rod. Thanks to the demagnetizing field, this is also true in the transverse direction whatever the value of $\chi > 0$. But in the axial direction, quite the contrary happens when $\chi \ge 2$: each cross-section of the rod is influenced by both the close and distant magnetized parts of the rod. As a conclusion, our experiments demonstrated that the "axial model" describes more accurately the shape of nickel wires with $\chi > 100$ and also of microrods described here, although $\chi \sim 2^{11}$. It also better predicted the threshold of the field intensity at which the rod buckles. The constant axial part of the magnetization

⁷L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, Pergamon press, Oxford, 2nd edn, 1970.

⁸F. Gerbal, Y. Wang, F. Lyonnet, J. Bacri, T. Hocquet and M. Devaud, A refined theory of magnetoelastic buckling matches experiments with ferromagnetic and superparamagnetic rods, *Proc. Natl. Acad. Sci. U. S. A.*, 2015, **112**(23), 7135–7140.

⁹The bent rod can be approximated by several contiguous ellipsoids.

 $^{^{10}}$ See ref. 8.

 $^{^{11}\}mathrm{See}$ ref. 8.

is determined by the part of the rod which is the most influenced by the external field, *i.e.* the section most aligned with the external field. In the cantilevered configuration studied here, this is thus the tip of the rod. Using $H_{\parallel} = H_{0\parallel}$ (the demagnetizing factor is assumed to be null along the rod main axis as in the infinite cylinder), this writes $M_{\parallel} = \chi(H_{\parallel})H_{\parallel} = \chi(H_{\parallel})\sin [\theta(L)] H_0$. We also neglected $\Gamma_{m\perp}$ in front of $\Gamma_{m\parallel}$ because mathematically $\forall \chi, \chi_{\perp} < 2$ when $n_{\perp} = 1/2$. With these conditions the "independent model" described by equation (3) is replaced by:

$$C\frac{d^2\theta(l)}{dl^2} + \pi r^2 M_{\parallel} B_0 \cos\left[\theta(l)\right] = 0 \tag{4}$$

This "axial model" also presents a very convenient advantage: with the constancy of $M = M_{\parallel}$, follows the constancy of H and χ (see below). But for an accurate measure of χ we improve for this paper the "axial model" to take into account Γ_{\perp} which may account for~ 40% of Γ_m when χ is low. If neglected, the experiments described in the main text done for variable field strength and directions (Fig. 2) does not yield constant ϕ . Since \vec{H}_{\perp} always follows the "independence rule", the expression of $\Gamma_{m\perp}$ in equation (1) is valid and the torque balance of the complemented axial model becomes:

$$C\frac{d^{2}\theta(l)}{dl^{2}} + \left\{\chi(H_{\parallel})\sin(\theta_{L}) - \frac{\chi(H_{\perp})}{1 + \chi(H_{\perp})/2}\sin\left[\theta(l)\right]\right\}\cos\left[\theta(l)\right]\frac{\pi r^{2}B_{0}^{2}}{\mu_{0}} = 0$$
(5)

Without the assumption that $\chi(H)$ is constant, neither equation (3), nor (5) may be integrated. To circumvent these difficulties we performed very small deformation measurements (deflection $\delta \sim L/50 \sim 1 \ \mu\text{m}$) in order to keep almost constant the orientation of the rod with respect to the field. In this condition, we approximate in equation (5): $\sin[\theta(l)] \simeq \sin[\theta(L)]$.¹² This also allowed to consider H_{\perp} as constant in the rod, and thus also $\chi(H_{\perp})$ (Fig. S4). With these approximations, equation (5) may be integrated and yields the shape of the rod:

$$x(l) = 2\lambda \left\{ \sqrt{1 - \frac{\sin(\theta_0)}{\sin(\theta_L)}} - \sqrt{1 - \frac{\sin\left[\theta(l)\right]}{\sin(\theta_L)}} \right\}$$
(6)

 $[\]overline{\left[\frac{12\sin\left[\theta(l)\right]}{\sin\left[\theta(L)\right]} + \cos\left(\theta_L\right)\left(\theta(l) - \theta_L\right)\right)}$ With $\theta_L - \theta_0 \lesssim 3^\circ \ll \theta_0 = 55^\circ$ (see further), the approximation is better than 4%. Alternatively, replacing $\sin\left[\theta(L)\right]$ by $\sin\left[\theta(l)\right]$ yields the equation of the independent model (Eq. (3)). Indeed, with a small deformation, the infinite straight cylinder model holds to compute the internal magnetization. Thus, analytical integration of equation (3) is feasible and yields somewhat different expressions which are: $x(l) = \kappa \left[\arcsin\left(\frac{\sin\theta(l)}{\sin\theta_L}\right) - \arcsin\left(\frac{\sin\theta_0}{\sin\theta_L}\right) \right], \ y(l) = \kappa \left[\arccos\left(\frac{\cos\theta_0}{\cos\theta_L}\right) - \operatorname{arccosh}\left(\frac{\cos\theta(l)}{\cos\theta_L}\right) \right]$ and $L = \kappa \int_{\theta_0}^{\theta_L} \frac{d\theta'}{\sqrt{\sin^2\theta_L - \sin^2\theta'}}$ with $\kappa = \sqrt{\frac{\mu_0 C}{\pi r^2 \Delta \chi B_0^2}}$. Although this model does not match the rod shape as well as the "axial model", they are very similar for small deflections. In this case, both models yield similar values for the volume fraction ϕ .

$$y(l) = \lambda \int_{\theta_0}^{\theta(l)} \frac{\sin(\theta) d\theta}{\sqrt{1 - \frac{\sin(\theta)}{\sin(\theta_L)}}}$$
(7)

with $\lambda = \sqrt{\frac{\mu_0 C}{2\pi r^2 \Delta \chi B_0^2}}$. From equations (6) and (7), we deduce the relation between L and θ_L :

$$L = \lambda \int_{\theta_0}^{\theta_L} \frac{d\theta}{\sqrt{1 - \frac{\sin(\theta)}{\sin(\theta_L)}}}$$
(8)

as well as the deflection of the tip:

$$\delta = -\sin(\theta_0)x(L) + \cos(\theta_0)y(L) \tag{9}$$

From the experimental measurements of L and δ , we numerically solved equations (8) and (9) to find θ_L and λ from which follows $\Delta \chi$. Equation (8) always admits a solution for $\theta_L \ge \theta_0 > 0$. But in the case $\theta_0 = 0$, a solution exists only if $L \ge 2\lambda$. This is the mathematical translation of the magnetoelastic buckling instability which occurs at the critical field $B_c = \frac{1}{rL} \sqrt{\frac{2\mu_0 C}{\pi \Delta \chi}} \simeq \frac{1}{rL} \sqrt{\frac{2\mu_0 C}{\pi \chi (H_{0\parallel_L})}}$ in the axial model ¹³.

From $\Delta \chi$ and the geometrical parameters, one can compute $\chi(H_{\parallel})$ and $\chi(H_{\perp})$, each of them being proportional to the magnetic susceptibility of the nanoparticles which compose the rods, *i.e.* $\chi(H_{\parallel(\perp)}) = \frac{\phi}{\phi^v} \chi^v(H_{\parallel(\perp)})$. Using the expression of $\Delta \chi$ and the data $\chi^v(H)$, ϕ could thus be obtained by solving numerically the set of equations:

$$H_{\parallel} = H_{0\parallel} \qquad H_{\perp} = \frac{H_{0\perp}}{1 + \frac{\phi}{\phi^v} \chi^v(H_{\perp})/2}$$
 (10)

$$\phi = \phi^v \frac{\Delta \chi}{\chi^v(H_{0\parallel}) - \chi^v(H_{\perp}) \frac{H_{\perp}}{H_{0\perp}}}$$
(11)

based on these latter equations, Fig. S4 shows the variation of the magnetic susceptibilities in a infinitely-long cylinder as a function of the field components, which depends themselves on the induction field angle with respect to the cylinder.

 $^{^{13}\}mathrm{See}$ ref. 8.

ESI, Figure S4:

Rod magnetic susceptibilities as a function of the incidence angle of the field



Fig. S4 Rod magnetic susceptibilities as a function of the incidence angle of the field. Computation of the magnetic susceptibilities of an infinitely long rod (with a particle volume fraction $\phi^v = 15\%$) as a function of its orientation α in respect with the external induction field $B_0 = 5$ mT (see inset). The various susceptibilities are numerically computed from equations (10) and (11) and after the VSM data $\chi^v(H)$. H_{\parallel} and H_{\perp} are respectively the axial and orthogonal components of the magnetic field inside the rod, $\Delta \chi = \chi(H_{\parallel}) - \chi_{\perp}(H_{\perp})$ with $\chi_{\perp} = \frac{\chi}{1+\chi/2}$. Interestingly, $\Delta \chi$ varies dramatically by almost a factor of 5 when α is rotated by 90° but varies by less than 10% for α between 0 and 20°.

ESI, Fig. S5: Elastic and plastic deformations of the rods



A: deflection distance δ of a 44.6 µm long cantilever rod during a typical sequence of magnetic measurements with an applied induction field. The field is alternatively turned on for 700 ms (including 200 ms of camera acquisition) and off (for the same time) to check its elastic return to its undeformed state. The field is always applied at 35°, at increasing strength (3.26, 5.59 and 7.61 mT) and 5 times for each strength to test the reproducibility and average out the variations of the deflected amplitude due to thermal fluctuations. B: by contrast, a strong induction field (33.7 mT) applied for a long time yields large non-elastic deformations. The arrow indicates the time at which the field is turned off. The recording has been stopped but the rod does not return to the initial state ($\delta = 0$) even after hours.

ESI, Movie 1: automatic recognition of the deflected rod centerline by the image recognition software

Movie made of 31 time-laps reflection images of a 53 µm long rod deflected by an increasing magnetic field successively turned on and off according to the experimental procedure shown on ESI[†], Fig. S5. Lower left bar=10 µm. The direction of the field is indicated by the upper right arrow $(\theta_0 = 35^\circ)$ and its intensity written on the movie. The dark line drawn on the middle of the rod image is its centerline automatically digitized by our software.