Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information for "Dissipative Non-Equilibrium Dynamics of Self-Assembled Paramagnetic Colloidal Clusters"

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1 Measurement of magnetic susceptibility

We have performed a direct measurement of the magnetic susceptibility χ of the particles to verify the values reported in the literature.[1] In the experiment, we have tracked the distance between two particles far from any other particle under the action of a vertical static magnetic field. Balance between particle repulsion and viscous friction, which we suppose dominated by Stokes drag, leads to the theoretical prediction of the interparticle radial velocity:

$$v = \frac{\mathrm{d}r}{\mathrm{d}t} = \frac{2B^2}{9\eta\mu_0}\chi^2\frac{a^5}{r^4}, \tag{S1}$$

where B is the magnitude of the field, η the fluid's dynamic viscosity, μ_0 the vacuum permeability, a the particle radius, and r the interparticle distance. We fit this law to measurements of $v = f(r)$ for both particle types, M-450 and M-270, as shown in Fig. S1. The experiment is repeated for 20 particle pairs of each type. The experiments are performed under two different field magnitudes for the two particle sizes ($B = 1$ mT for M-450 and $B = 4$ mT for M-270) in order to keep an approximately constant value of $\Gamma_{\mathrm{mag}} = U_{\mathrm{mag}}/(k_{\mathrm{B}}T)$. Nevertheless, similar estimates of χ_1 and χ_2 are obtained if the experiments are performed at constant $B = 1$ mT (not shown). The slope of the fits is constrained by the theoretical prediction $v \propto r^{-4}$, whereas the intersect of each fit with the vertical axis provides the estimate of χ. The resulting estimates of the magnetic susceptibilities are $\chi_1 = 1.15$ (M-450 particles) and $\chi_2 = 0.64$ (M-270 particles), whereas the literature values are 1.63 and 0.76, respectively.[1] The difference may be due to the fact that our values are obtained by neglecting solid friction, which is actually non-negligible. Moreover, particle diffusion in our experiments is significant and introduces large experimental variability, as shown by the large error bars in Fig. S1. We note that in measuring $v = f(r)$ we have corrected for the diffusive effect on radial velocity v by measuring the particle displacement along the initial interparticle direction, and not as the increase in interparticle distance, which would lead to a overestimate of v due to particle diffusion.

The key parameter when comparing our theoretical model of the dynamics of cluster rotation to the experiments presented in the main article is the ratio of magnetic susceptibilities, χ_1/χ_2. The value of this ratio is 1.80 for our experimental estimates and 2.14 for the literature values used in the article. Changing the value of this ratio will lead to changing Fig. 4(b) in the main article, which would look as shown in Fig. S2.

The normalization remains satisfactory for the experimentally obtained value of the ratio χ_1/χ_2, but it is less good than using the literature values. Because of the significant uncertainty in our direct determination of the values of χ due to the reasons explained above, in the main article we have used the values of χ reported in the literature.

2 Theoretical models

2.1 Dynamics of cluster rotation

The dipolar line tension acting at the edge of the two-dimensional cluster is[2]

$$\lambda_{\mathrm{dip}} = \lambda_{\mathrm{is}} + \lambda_{\mathrm{anis}} \cos(2\Phi) , \tag{S2}$$

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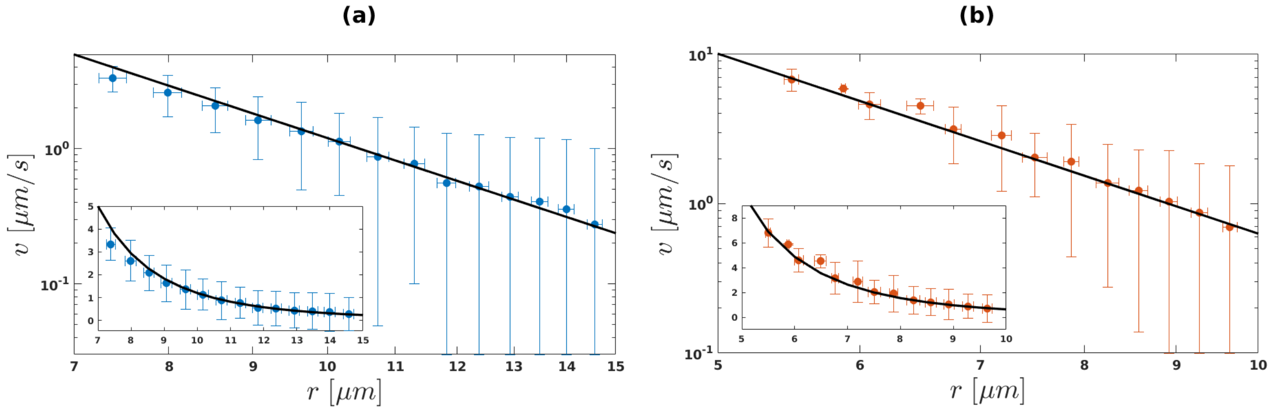

Figure S1: Experimental measurement of the radial velocity v between two identical paramagnetic particles repulsing each other under the action of a vertical static magnetic field of magnitude B, as a function of the interparticle distance r. Plot **(a)** corresponds to M-450 particles ($B = 1$ mT) and plot **(b)** to M-270 particles ($B = 4$ mT). Error bars are standard errors. The black line is the theoretical prediction, with the predicted slope $v \propto r^{-1/4}$ and a vertical offset fitted to the data. The figures are presented as a log-log plot, whereas the insets show the same data using linear axes.

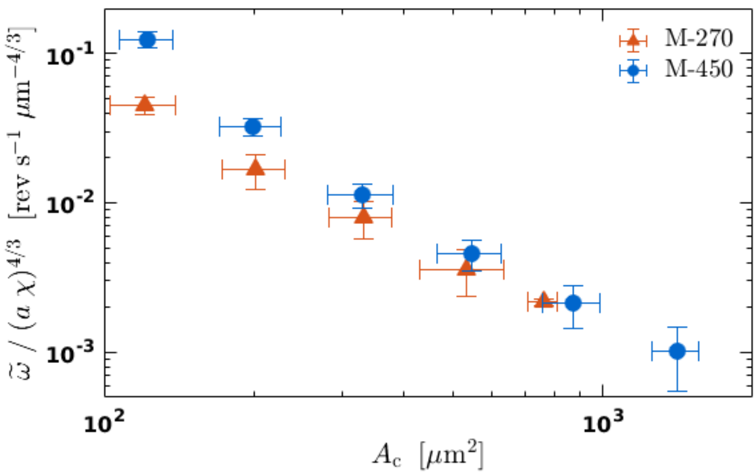

Figure S2: Redrawing of Figure 4b of the article, using the experimentally measured value of $\chi_1/\chi_2 = 1.80$ instead of the value reported in the literature and used in the main text ($\chi_1/\chi_2 = 2.14$).

where Φ is the in-plane angle between the magnetic field and the vector normal to the cluster boundary. $\lambda_{\rm is}$ and $\lambda_{\rm anis}$ are defined as follows:

$$\lambda_{\rm is} = -\frac{1}{2\pi}\mu_0 \tilde{M}^2 \ln\left(\frac{8R_{\rm c}\sqrt{n}}{e}\right) P_2(\cos\theta) \tag{S3}$$

$$\lambda_{\rm anis} = \frac{3}{4\pi}\mu_0 \tilde{M}^2 \ln\left(\frac{8R_{\rm c}\sqrt{n}}{e^{7/3}}\right) \sin^2\theta \ , \tag{S4}$$

where P_2 is the second Legendre polynomial, $\tilde{M} = nV_{\rm p}\chi B/\mu_0$ is the cluster's magnetization per unit area in the continuum approximation, with $n = 1/(2\sqrt{3}a^2)$ the 2D particle density in a cluster, $V_{\rm p} = 4\pi a^3/3$ is the particle volume, and χ is the magnetic susceptibility of a particle.

The cluster is subjected to two torques, magnetic and viscous. The magnetic torque is

$$\tau_{\rm m} = V_{\rm c} B^2 \sin^2(\theta)\chi''_{\rm eff}/\mu_0 \ , \tag{S5}$$

where $\chi''_{\rm eff} = 3\pi a u''_r/8R_{\rm c}^2$ is the imaginary part of the effective magnetic susceptibility, and $V_{\rm c} = \pi R_{\rm c}^2\, 2a$ is the cluster volume. The viscous torque is

$$\tau_{\rm visc} = f\eta_{\rm w} R_{\rm c}^3 \omega \ , \tag{S6}$$

where $f = A\pi R_{\rm c}\omega^{1/2}/(2\nu_{\rm w}^{1/2})$ is the hydrodynamic drag coefficient of the cluster, assimilated to a rotating flat disk near a wall,[3] with $\eta_{\rm w}$ and $\nu_{\rm w}$ the dynamic and kinematic viscosities of water, respectively.

Balancing the two torques above gives:

$$u''_r = \frac{8\,\mu_0\, f\,\eta_{\rm w} R_{\rm c}^5\omega}{3\,\pi\ \ a\, V_{\rm c}\, B^2\, \sin^2\theta}. \tag{S7}$$

By solving the elasticity equation, $-\boldsymbol{\nabla} p + G_{\rm c}\boldsymbol{\Delta u} = 0$, we find the following expression of the radial component of the dynamic cluster deformation:[2]

$$u_r = \frac{-2\lambda_{\rm anis} R_{\rm c}}{3(\lambda_{\rm is} + G_{\rm c}R_{\rm c})}\exp\left(-2i\Phi\right) \ . \tag{S8}$$

Inserting the complex shear modulus, $G_{\rm c} = G'_{\rm c} - iG''_{\rm c}$, into Eq. (S8) gives:

$$u_r = \frac{-2\lambda_{\rm anis} R_{\rm c}\ [(\lambda_{\rm is} + G'_{\rm c}R_{\rm c}) + i\ G''_{\rm c}R_{\rm c}]}{3[(\lambda_{is} + G'_{\rm c}R_{\rm c})^2\ +\ G''^2_{\rm c}R_{\rm c}^2]}\exp\left(-2i\Phi\right) \ , \tag{S9}$$

where the imaginary part of the radial distortion is:

$$u''_r = \frac{2\lambda_{\rm anis} G''_{\rm c} R_{\rm c}^2}{3[(\lambda_{\rm is} + G'_{\rm c}R_{\rm c})^2\ +\ G''^2_{\rm c}R_{\rm c}^2]} \ . \tag{S10}$$

Cluster viscoelasticity is described by the Kelvin-Voigt model, $G_{\rm c} = K - 2i(\Omega - \omega)\eta_{\rm c}$. Thus, the imaginary part of the radial distortion becomes:

$$u''_r = \frac{4\lambda_{\rm anis}(\Omega - \omega)\eta_{\rm c} R_{\rm c}^2}{3[(\lambda_{\rm is} + KR_{\rm c})^2\ + 4\ (\Omega - \omega)^2\eta_{\rm c}^2 R_{\rm c}^2]} \ . \tag{S11}$$

By considering that $\Omega \gg \omega$, $\lambda_{\rm is} \ll KR_{\rm c}$, and $\eta_{\rm c}\Omega \ll K$, Eq.(S11) becomes:

$$u''_r \approx \frac{4\lambda_{\rm anis}\Omega\eta_{\rm c}}{3K^2} \ . \tag{S12}$$

By inserting Eq.(S12) into Eq.(S7), we find the following expression of the cluster's angular velocity:

$$\omega^{3/2} = \frac{4\pi^2}{18A\mu_0^2}\frac{\sqrt{\nu_{\rm w}}}{\eta_{\rm w}}\eta_{\rm c}\sin^4\theta\ \ln\left(\frac{2^{5/2}}{3^{1/4}e^{7/3}}\frac{R_{\rm c}}{a}\right)\ \frac{a^4\chi^2}{K^2R_{\rm c}^4}\Omega\ B^4 \ , \tag{S13}$$

We postulate that the dominant contribution to the storage shear modulus, $G_{\mathrm{c}} = K$, arises from steric interactions (see Eq. (3) and discussion in the main manuscript). Then, we find that the 2D elastic modulus of the cluster, K, is expressed as

$$K = C\,a/\ln(R_{\mathrm{c}}/a)\ . \tag{S14}$$

By inserting the Eq.(S14) into Eq.(S13), we obtain our final expression of the cluster's angular velocity:

$$\omega = \gamma\ \ln^{2/3}\left(\frac{2^{5/2}}{3^{1/4}e^{7/3}}\frac{R_{\mathrm{c}}}{a}\right)\ln^{4/3}\left(\frac{R_{\mathrm{c}}}{a}\right)\ \frac{(a\chi)^{4/3}}{R_{\mathrm{c}}^{8/3}}\Omega^{2/3}\ B^{8/3}\ , \tag{S15}$$

with $\gamma \equiv \left[\frac{4\pi^2}{18A\mu_0^2}\frac{\sqrt{\nu_{\mathrm{w}}}}{\eta_{\mathrm{w}}}\frac{\eta_{\mathrm{c}}}{C^2}\sin^4\theta\right]^{2/3}$.

2.2 Disassembly dynamics

The conservation equation of particles is

$$\frac{\partial\rho}{\partial t} + v\frac{\partial\rho}{\partial r} = -\rho\left(\frac{v}{r} + \frac{\partial v}{\partial r}\right)\ . \tag{S16}$$

In the mean-field approach, the dipolar potential energy of a particle i located at a distance r from the cluster's center is defined as:

$$U_{\mathrm{dip}} = \frac{1}{2}\sum_{j\neq i} U_{ij}^{\mathrm{dip}}\ , \tag{S17}$$

with $U_{ij}^{\mathrm{dip}} = \frac{\mu_0}{4\pi}\frac{\chi_{\mathrm{V}}^2 B^2}{l_{ij}^3}$ is the pair potential of two parallel identical dipoles, where l_{ij} is the distance between the two dipolar particles i and j, and $\chi_{\mathrm{V}} = \chi V_{\mathrm{p}}/\mu_0$ with V_{p} the particle volume. Assuming a triangular lattice with lattice constant $l(r)$, the local density at a distance r from the cluster's center is given by:

$$\rho(r) = 2/[\sqrt{3}\,l(r)^2]\ , \tag{S18}$$

By performing the sum in Eq.(S17) and using Eq.(S18), it has been shown that the dipolar potential energy depends on the local density as:[4]

$$U_{\mathrm{dip}} = \frac{2M}{5}\frac{\mu_0}{4\pi}\chi_{\mathrm{V}}^2 B^2 \rho(r,t)^{3/2}\ , \tag{S19}$$

where $M \approx 11.116$ is a geometrical constant obtained by the sum of dipolar interactions among all particles in an hexagonal lattice.[4]

Each particle is subjected to a radial magnetic force $F = -\partial U_{\mathrm{dip}}/\partial r$ and to viscous friction, so that its radial velocity is $v = F/\xi$, with ξ the friction coefficient. Using the result given by Eq. (S19), we obtain

$$v = -\frac{\rho^{1/2}}{\beta}\frac{\partial\rho}{\partial r}\ , \tag{S20}$$

with $\beta = (20\pi\xi)/(3M\mu_0\chi_{\mathrm{V}}^2 B^2)$. Equation (S16) becomes:

$$\beta\frac{\partial\rho}{\partial t} = \rho^{3/2}\frac{\partial^2\rho}{\partial r^2} + \frac{1}{r}\rho^{3/2}\frac{\partial\rho}{\partial r} + \frac{3}{2}\rho^{1/2}\left(\frac{\partial\rho}{\partial r}\right)^2\ , \tag{S21}$$

with boundary conditions $\mathrm{d}\rho/\mathrm{d}r = 0$ at $r = 0$ and $\rho(R) = 0$, where R is the cluster radius (note that $R(t=0) = R_{\mathrm{c}}$).

To solve Eq. (S21), we assume that the density profile can be factorized as:

$$\rho(r,t) = \rho_0(t)y(x)\ , \tag{S22}$$

where $\rho_0(t) = \rho(0,t)$ is the density at the cluster center, and $x = r/R(t)$ is the dimensionless radial distance. The conservation law of the total number of particles,

$$N = \int_0^R \rho(r,t) 2\pi r dr = \pi \rho_0 R(t)^2 I \ , \tag{S23}$$

yields:

$$\rho_0(t) = \frac{N}{\pi I} \frac{1}{R(t)^2}, \tag{S24}$$

where $I \equiv \int_0^1 2y(x) x \, \mathrm{d}x$. Therefore, Eq. (S21) can be written as:

$$-2\beta \left(\frac{\pi I}{N}\right)^{3/2} R^4 \frac{\partial R}{\partial t} = \left[y^{1/2} y'' + y^{1/2} \frac{y'}{x} + \frac{3}{2} y^{-1/2} (y')^2 \right] \left[1 + \frac{x y'}{2y} \right]^{-1} = -\alpha \ , \tag{S25}$$

where α is a separation constant. The temporal factor in Eq. (S25),

$$2\beta \left(\frac{\pi I}{N}\right)^{3/2} R^4 \frac{\partial R}{\partial t} = \alpha \ , \tag{S26}$$

has the following exact solution:

$$R(t)^5 = R_c^5 + \frac{5\alpha}{2\beta} \left(\frac{N}{\pi I}\right)^{3/2} t \ . \tag{S27}$$

The spatial factor in Eq.(S25) is:

$$\left[y^{1/2} y'' + y^{1/2} \frac{y'}{x} + \frac{3}{2} y^{-1/2} (y')^2 \right] \left[1 + \frac{x y'}{2y} \right]^{-1} = -\alpha \ , \tag{S28}$$

with the following boundary conditions: $y(0) = 1$, $\mathrm{d}y/\mathrm{d}x = 0$ at $r = 0$, and $y(1) = 0$. The exact solution of this equation is:

$$y(x) = (1 - x^2)^{\alpha/4} \ , \tag{S29}$$

with $\alpha = 8/3$.

3 Supplementary Movies

Supplementary Movie 1
Self-assembly of paramagnetic particles (Dynabeads M-450) sedimented on the xy plane under a rotating magnetic field contained in the plane ($B = 1$ mT, $\Omega = 2960$ Hz). The movie shows the beginning (1 minute) and the end (1 minute) of a 10-minute experiment, and it is accelerated 4 times. The scale bar corresponds to 200 μm.

Supplementary Movie 2
Disassembly of a paramagnetic particle cluster (Dynabeads M-450) contained in the xy plane under a constant field acting along the z direction ($B = 0.9$ mT). The field is switched on at the beginning of the movie ($t = 0$) and kept constant throughout. The movie is accelerated 4 times. The scale bar corresponds to 20 μm.

References

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