Field-Controlled Assembly and Structural Transitions in Shifted-Dipole Trimer Clusters: ESPResSo Simulations and Order-Parameter Analysis

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July 6, 2025

Contents

Abstract

Ferrofluids (magnetic *nanoparticles*) and magnetorheological fluids (magnetic *microparticles*) are suspensions of magnetic, sub-micron objects in a non-magnetic carrier liquid. Janus or magnetically capped colloids add a built-in dipolar *anisotropy*: the magnetic moment is displaced from the particle centre. We simulate such particles with a lightweight *shifted-dipole* model and ask two questions: 1) Can this minimal model *qualitatively* reproduce the field-induced ring-to-chain transitions observed experimentally in trimer clusters? 2) How do thermal fluctuations modify the $T = 0$ ground-state predictions by Kantorovich *et al.* [1]?

Using Brownian-dynamics simulations in ESPResSo and an orientational order parameter S, we show that increasing the dimensionless dipole shift a drives a clear progression from linear ($S \approx 1$) to bent/triangular configurations ($S \approx 0.59$) and finally to bistable, quantised structures. Thermal noise shifts the transition boundaries relative to the athermal theory, demonstrating its decisive role in real systems.

1. Introduction

1.1. Experimental motivation

Magnetically capped silica spheres—often called *Janus magnetic colloids*—consist of a silica core half-coated with a thin ferromagnetic Co/Pd layer [2]. Trimers of these particles exhibit two dominant self-assembly motifs (Fig. 1.1): a flux-closure *ring* with zero net moment and a staggered *chain* with finite magnetisation. Pulsated external fields repeatedly break and re-form the clusters, offering a stringent test for simulation models.

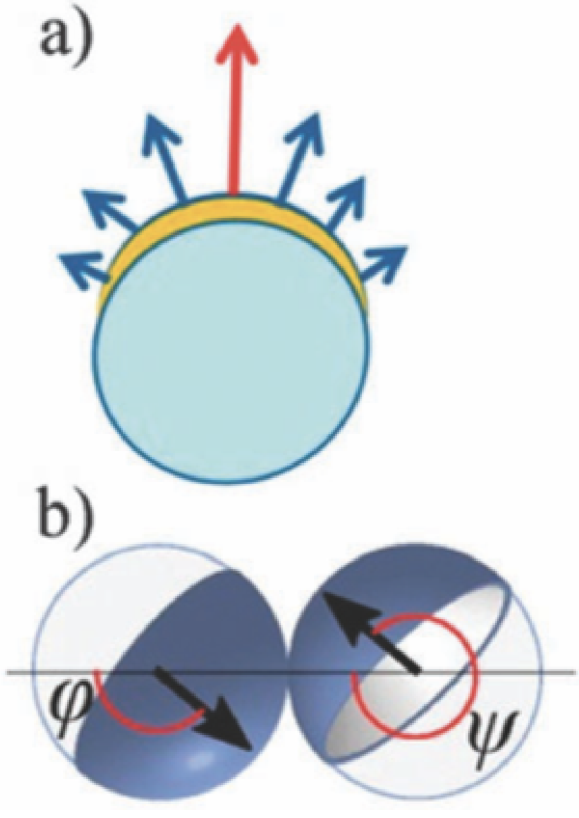

Figure 1.1.: **Sketches and microscopy images of self-assembled structures from magnetic Janus particles.** (a) Cross-section sketch of a silica sphere with hemispherical metal coverage (yellow arc). Arrows indicate the magnetization distribution. (b) Sketch of two particles in contact, displaying the cap (dark blue) and the net magnetic moment (black arrow), which has an in-plane orientation measured by the angles ϕ and θ. (Adapted from [2].)

1.2. Project motivations

1. **Minimal modelling of asymmetric dipoles.** The *shifted-dipole* (sd) model places a point dipole a distance d from the sphere centre, giving a dimensionless offset $a = d/R$. Its simplicity enables dynamic simulations of dozens of particles—far cheaper than micromagnetic approaches—yet it preserves the key asymmetry of Janus particles.

2. **Thermal fluctuations.** Ground-state studies at $T=0$ predict a sequence of ring $\rightarrow$ anti-parallel structures with increasing a [1]. Experiments, however, run at room temperature. Quantifying how finite kT modifies those boundaries is the core scientific question of this project.

1.3. Paper outline

Section 2 introduces the sd-particle model and interaction potentials. Section 3 details the ESPResSo setup, parameter mapping, and simulation protocol. The order parameter S is defined in Sec. 3.5. Results (Sec. 4) combine histograms of $P(S)$ with VMD snapshots; Sec. 5 summarises implications and future work.

2. Model

2.1. Shifted-dipole particle

A particle of radius R carries a point dipole $\boldsymbol{\mu}$ fixed at a distance d from its geometric centre, defining the control parameter

$$a = \frac{d}{R}. \tag{2.1}$$

The sd-model mimics the off-centred magnetisation of Janus spheres or core–shell particles.

2.2. Interaction potentials

Dipole–dipole interaction. ESPResSo computes pair energies

$$U_{\mu\mu}(ij) = \frac{\mu_0}{4\pi r_{ij}^3}\Big[\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j - 3(\boldsymbol{\mu}_i\cdot\hat{\mathbf{r}}_{ij})(\boldsymbol{\mu}_j\cdot\hat{\mathbf{r}}_{ij})\Big], \tag{2.2}$$

where $\hat{\mathbf{r}}_{ij}$ is the unit vector between dipoles i and j.

Excluded volume. Real–real particle pairs interact via the Weeks–Chandler–Andersen repulsion

$$U_{\mathrm{WCA}}(r) = \begin{cases} 4\epsilon\Big[(\sigma/r)^{12} - (\sigma/r)^6\Big] + \epsilon, & r \le 2^{1/6}\sigma, \\ 0, & r > 2^{1/6}\sigma, \end{cases} \tag{2.3}$$

with $\sigma = d^*$ in simulation units.

Zeeman torque. An external homogeneous magnetic field $\mathbf{B}$ exerts a torque on each dipole,

$$\boldsymbol{\tau}_i = \boldsymbol{\mu}_i \times \mathbf{B}, \tag{2.4}$$

where $\mathbf{B} = \mu_0\mathbf{H}$ and μ_0 is the permeability of free space.

3. Methods

3.1. Particle and interaction parameters

Core parameters

- **Dimensionless particle diameter** d^*: 2.0, providing a standardised scale for particle interactions.
- **Dimensionless dipole magnitude** μ^*: 10.0, chosen to strongly manifest dipolar interaction effects.
- **Shift parameter** $a = d/R$: systematically varied over $\{0.0, 0.1, \ldots, 0.8\}$ to probe distinct structural regimes.
- **Thermal energy** kT^*: 0.01, ensuring thermal fluctuations are neither negligible nor dominant.
- **Friction coefficients** (γ_t^*, γ_r^*): derived from dimensional scaling to guarantee realistic Brownian dynamics.

Simulation box and boundary conditions

- A cubic box of size $10 \times 10 \times 10$ (simulation units) with non-periodic boundaries isolates the quasi-2D trimer system and avoids spurious image interactions.

Particle initialization and placement

- Trimers are initialized within an annulus of inner radius $R_{\text{min}} = 1.5$ and outer radius $R_{\text{max}} = 3.0$.
- A minimum centre–centre distance $D_{\text{min}} = 1.2$ prevents initial overlaps.
- Initial orientations are fully randomised via quaternion rotations to assure unbiased sampling.

3.2. Parameter Mapping

To bridge simulations and experiments, we define clear mappings between physical quantities and dimensionless simulation parameters. The following tables summarize the scales and dimensionless parameters employed.

Physical Parameters

- **Particle diameter ($d_{\mathbf{phys}}$):** 4.54×10^{-6} m
- **Thermal energy ($kT_{\mathbf{phys}}$):** 4.10×10^{-21} J
- **Dipole moment ($\mu_{\mathbf{phys}}$):** 5.94×10^{-14} A $\cdot$ m^2
- **Translational friction ($\gamma_{t,\mathbf{phys}}$):** 1.04×10^{-7} kg/s
- **Rotational friction ($\gamma_{r,\mathbf{phys}}$):** 7.0×10^{-19} J $\cdot$ s

Dimensionless Parameters

- **Dimensionless particle diameter (d^*):** 2.0
- **Dimensionless thermal energy (kT^*):** 0.01
- **Dimensionless dipole moment (μ^*):** 10.0
- **Dimensionless translational friction (γ_t^*):** 3.135×10^3
- **Dimensionless rotational friction (γ_r^*):** 4.095×10^3
- **Time scale ($T_{\mathbf{vis}}$):** 0.01/24 s

Unit Conversion Scales

Table 3.1.: Unit conversion scales used for physical to dimensionless mapping.

Quantity	Symbol	Value
Length scale	L	2.270×10^{-6} m
Time scale	T	4.167×10^{-4} s
Energy scale	E_{scale}	4.103×10^{-19} J
Mass scale	M	1.382×10^{-14} kg
Current scale	A	1.152×10^{-3} A

3.3. Brownian dynamics integrator

ESPResSo integrates the over-damped Langevin equations

$$\gamma_t^* \,\dot{\mathbf{r}}_i = -\nabla_{\mathbf{r}_i} U + \boldsymbol{\eta}_i(t), \qquad \gamma_r^* \,\dot{\boldsymbol{\theta}}_i = \boldsymbol{\tau}_i + \boldsymbol{\xi}_i(t), \tag{3.1}$$

where U is the total potential (Eqs. 2.2–2.3) and the stochastic forces $\boldsymbol{\eta}, \boldsymbol{\xi}$ satisfy fluctuation–dissipation [5].

3.4. Simulation protocol

After 5×10^5 equilibration steps without field, the system undergoes five ON/OFF cycles (ON: 2×10^5 steps, OFF: 4×10^6 steps). Sampling is restricted to the final 20 % of each OFF block.

3.5. Order parameter S

For particle i, let $\mathbf{m}_i$ be its dipole unit vector and $\mathbf{r}_{i1}, \mathbf{r}_{i2}$ the unit vectors to its two neighbours. The local alignment is

$$A_i = \frac{1}{2}\Big[\max(\mathbf{m}_i\cdot\mathbf{r}_{i1}, \mathbf{m}_i\cdot{-\mathbf{r}_{i1}}) + \max(\mathbf{m}_i\cdot\mathbf{r}_{i2}, \mathbf{m}_i\cdot{-\mathbf{r}_{i2}})\Big], \tag{3.2}$$

and the trimer order parameter is

$$S = \frac{A_1 + A_2 + A_3}{3}. \tag{3.3}$$

$S \approx 1$ indicates a straight chain; $S \approx 1/\sqrt{2}$ corresponds to an equilateral ring.

3.6. Trajectory data and analysis

Trajectory data (positions and orientations) are recorded in VTF (Visual Molecular Dynamics trajectory) format throughout each simulation run. These files underpin all post-processing steps, most notably the construction of histogrammed order-parameter distributions $P(S)$ and the visual identification of chain-like, triangular, or anti-parallel motifs.

In summary, our computational model and ESPResSo-based methodology constitute a robust and flexible framework for systematically probing structural transitions in shifted-dipole clusters, bridging theoretical predictions and experimental observations.

4. Results and Discussion

4.1. Histogram evolution of the order parameter $P(S)$

Figure 4.1 gathers the probability distributions $P(S)$ for all eight shift values a.

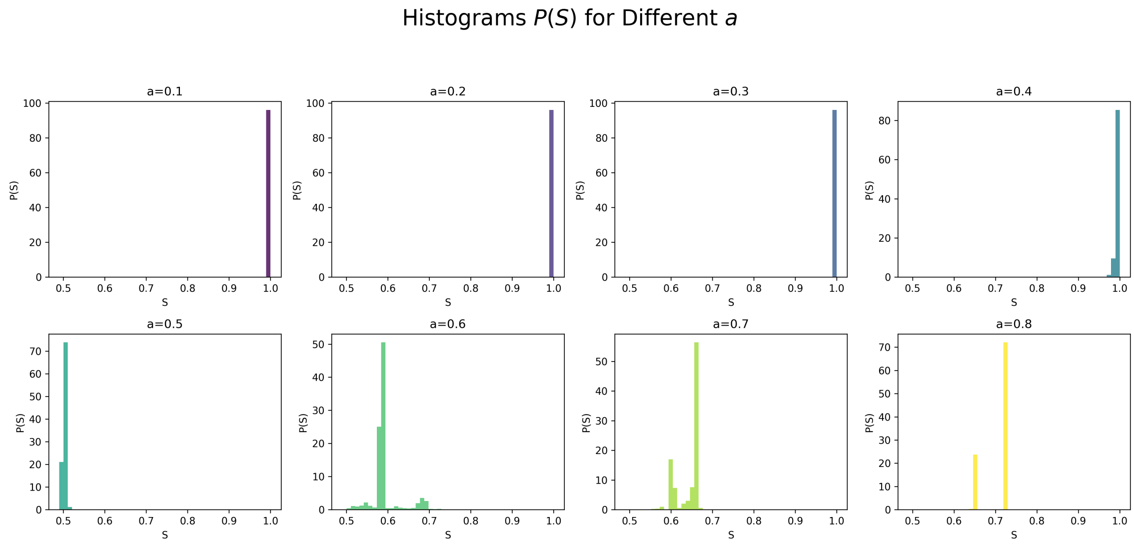

Figure 4.1.: Histograms of the order parameter S for all simulated shift values a. Each peak indicates the most probable trimer motif for a given a.

Three regimes are evident:

1. **Linear–chain regime** ($a \leq 0.3$). A sharp peak at $S \approx 1$ confirms that head-to-tail alignment dominates, in agreement with the $T{=}0$ ground-state prediction of Kantorovich *et al.* [1].

2. **Disordered transition window** ($0.4 \lesssim a \lesssim 0.55$). The peak flattens and broadens; the system explores a continuum of bent geometries. The maximal entropy point (mode at $S \approx 0.50 \pm 0.03$) occurs at $a \simeq 0.5$, slightly *smaller* than the athermal crossover, illustrating the softening effect of finite kT.

3. **Quantised–bent regime** ($a \geq 0.6$). The distribution collapses into one ($a = 0.6$) or two ($a \geq 0.7$) narrow peaks centred at $S \approx 0.59$. These correspond to the triangular "up–down–up" (or its mirror) state first seen in ground-state calculations, now stabilised by thermal activation barriers.

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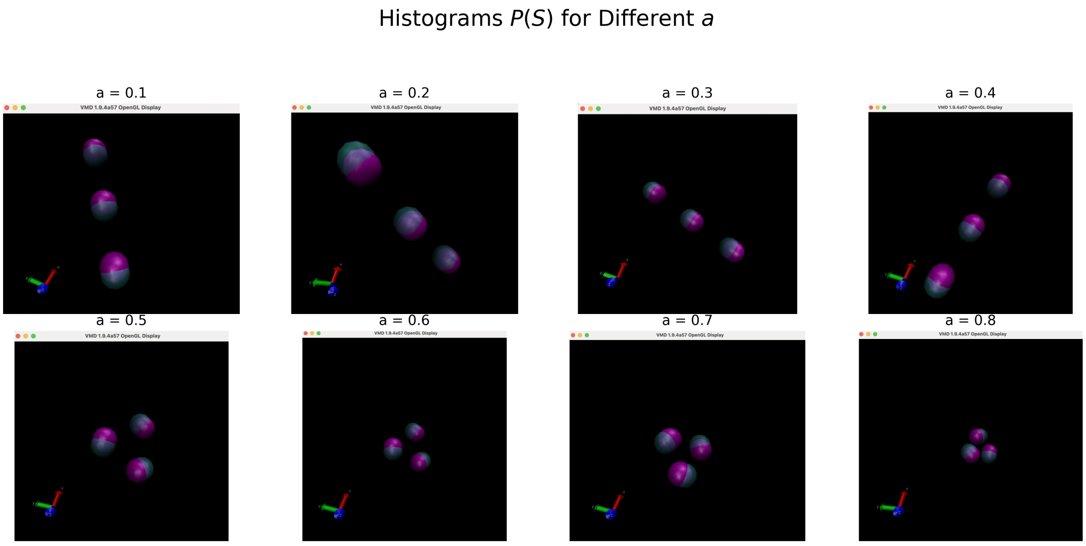

Figure 4.2.: VMD snapshots at modal order parameter S for each shift parameter a. Linear, bent, and triangular trimer motifs appear as a increases.

4.2. Representative configurations

Figure 4.2 shows VMD snapshots at the modal S value for each a.

- **Chains** ($a \leq 0.3$). Dipoles point head-to-tail; the virtual sites align on a common axis. No out-of-plane bending is observed during field-OFF sampling.
- **Floppy bent trimers** ($a = 0.5$). Thermal kicks overcome the shallow energy landscape, producing a fan of semi-bent states and hence the broad histogram.
- **Locked triangular states** ($a \geq 0.6$). Each particle forms a 120° angle with its neighbours; dipoles alternate "up–down–up" around the ring, minimising Eq. (2.2) while satisfying the excluded-volume constraint (2.3).

5. Conclusions

- The shifted-dipole model, fitted to experimental parameters, reproduces the *qualitative* ring-to-chain transition in Janus trimer experiments.
- Thermal fluctuations widen and shift the transition window, underscoring the importance of finite-temperature dynamics in designing field-programmable colloidal materials.

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A. ESPResSo Simulation Code Snippet

```
# ------------------------------
# Main simulation
# ------------------------------
def run_simulation_with_field_cycles(w_shift, vtf_name):
    # 1. System initialization
    system = espressomd.System(box_l=[10.0]*3)
    system.time_step = 0.01
    system.cell_system.skin = 0.4
    system.periodicity = [False]*3
    system.virtual_sites = espressomd.virtual_sites.
        VirtualSitesRelative(have_quaternion=True)

    # 2. Add rings
    for _ in range(3):
        add_particle_ring_virtual(system, D_MIN, R_MIN, R_MAX,
            CENTER, DIP_MAG, w_shift)

    # 3. Interactions
    system.non_bonded_inter[0,0].wca.set_params(epsilon=100.0,
        sigma=2.0)

    # 4. Thermostat (Brownian dynamics)
    system.thermostat.set_brownian(
        kT=kT_dim,
        gamma=GAMMA_T,
        gamma_rotation=GAMMA_R,
        seed=seed
    )
    system.integrator.set_brownian_dynamics()

    # 5. Dipolar actor
    system.actors.add(DipolarDirectSumCpu(prefactor=1.0))

    # 6. Visualization radii
    radii = {0:1.0, 1:(0.5 if w_shift>0 else 1.0), 999:(0.5 if
        w_shift>0 else 1.0)}
```