Low energy states of a frustrated colloidal ice system

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Abstract: A colloidal ice is a system of interacting paramagnetic colloids which are arranged along a lithographic lattice of double wells such that the lattice geometry competes with the pair interactions and the system generates geometric frustration. In this work, I have used numerical simulations to study this system arranged along a square lattice, where particles are confined in double-well gravitational traps. The double wells are filled each with one particle, and under an external magnetic field the particles can pass the central hill of the traps but never escape from them. The applied field induces repulsive magnetic dipolar interactions and the system try to reach a low energy state. To analyze this state, I have varied the field amplitude, the cut-off distance of the magnetic dipolar interactions and the thermodynamic temperature. Of all of these parameters, I found that both the cut-off distance and the temperature do not influence significantly the evolution of the system towards the low energy states, here measured in terms of the fraction of vertices. In contrast, the field strength allow to reach the system ground state faster.

I. INTRODUCTION

In physics, the concept of frustration appears when a system is not able to satisfy competing interactions among its components. In other words, the local interaction energies of the elements of the system can't be minimized simultaneously due to geometrical constraints [3]. A simple widespread example of geometrical frustration is a configuration of three Ising spins set in the vertices of a triangle such that they all want to be oriented antiferromagnetically. Due to the geometric restriction imposed by the lattice, this configuration cannot be achieved so two of the spins will arrange ferromagnetically generating a frustrated bond, and consequently the energy of the system will not be able to be minimized [2].

Delving further into the topic, one of the most interesting examples of geometric frustration is the water ice, where each atom of oxygen is surrounded by four atoms of hydrogen forming a tetrahedral configuration. In this geometry, the low energy configuration is obtained when two of the hydrogen atoms are close to the central oxygen atom while the remaining two are close to the neighbor oxygen atoms. In this configuration, the atoms fulfill the 'ice rules' [3], which are a prescription for the minimization of the absolute value of the topological charge q associated to each vertex. This charge can be defined as the difference between the number of spins pointing towards the vertex center and the number of spin pointing out: $q = 2n - z$, where z is the coordination number of the lattice and n is the number of spins pointing inward [3]. In particular, for a square lattice, $z = 4$, this rules state that in each vertex, in order to minimize the energy of the interaction, two spins point inward and two spins point outward, so $|q| = 0$.

The system I have studied is a microscopic artificial spin ice that consists of an ensemble of interacting colloidal particles restricted in a 2-dimensional square lattice of gravitational traps (which is a plane projection of the 3-dimensional tetrahedron lattice). These traps are filled at one-to-one filling ratio by paramagnetic colloidal particles with adjustable interactions. The double-well traps are characterized by an elliptical shape and have a low central hill, so that confined particles have the same probability to stay in one of the two potential wells due to thermal fluctuations. With this configuration, we can associate to each trap an Ising-like spin which points from the free end to the well occupied by the particle, as it is shown in FIG. 1.

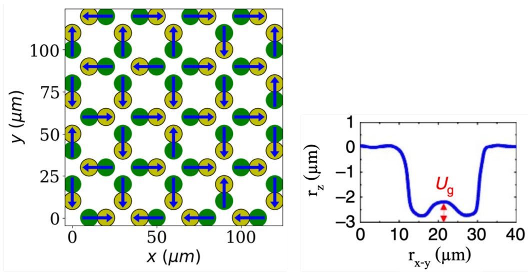

FIG. 1: ***Left*** **:**A square lattice with double-well traps, each of them containing a colloidal particle randomly placed in one of the two states, where the spins associated to each double well are represented as a blue arrow and point toward the end of the trap occupied by the particles. ***Right*** **:** cross-section of a gravitational trap with the central hill potential. Image reproduced from Ref.[2].

The paramagnetic colloids, when subjected to an external field, acquire a dipole moment and interact through repulsive dipolar forces. Thus, at a vertex four particle will try to repel each other in order to minimize the system energy. In this situation, the four pseudo-spins associated with the particle position point outward. However, when the particles are placed within a lattice it is not possible to minimize the energy of all the vertex's because there is a competition between the isotropic repulsive interaction of the particles and the geometric structure. As shown in FIG. 2, for a square lattice, there are sixteen possible vertex configurations that we can organize in four types depending on the associated value of the topological charge q. Although the spin interactions are not equivalent in type I and type II vertices, they obey the ice rule, where two spins point to the center of the vertex and two point out ($|q| = 0$). In type III we have three spins in and one out, and also one in and three out ($|q| = 2$). Finally, in the configurations of type IV we can find all spins pointing toward the vertex center or out ($|q| = 4$).

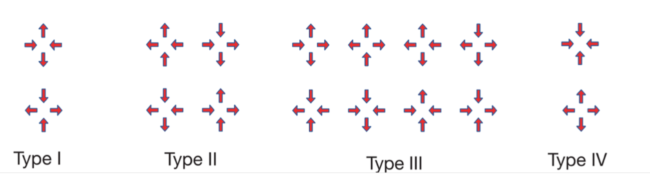

FIG. 2: Representation of the sixteen possible configurations of a vertex organized in four classes depending on their energy. We can note types I and II obey the ice rule (two spins in, two out). Image reproduced from Ref.[1].

To tune the pair interactions, the particles used in this system are magnetizable, and under an applied magnetic field $\mathbf{B}$, they acquire an induced dipole moment $\mathbf{m} = V\chi B/\mu_0$ pointing along the field direction [4]. Here V is the particle volume, χ is the magnetic volume susceptibility and μ_0 is the permeability of the medium. Consequently, if we apply an external magnetic field in the system, two particles (i, j) with induced moments $m_{i,j}$ and at positions $\boldsymbol{r}_{i,j}$ will interact through magnetic dipole forces and with an interaction potential [4] given by

$$U = -\frac{\mu_0}{4\pi}\frac{(\boldsymbol{m}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{m}_j \cdot \boldsymbol{r}_{ij})}{|\boldsymbol{r}_{ij}|^5} - \frac{(\boldsymbol{m}_i \cdot \boldsymbol{m}_j)}{|\boldsymbol{r}_{ij}|^3} \qquad (1)$$

This potential is maximally repulsive for dipole moments perpendicular to their separation distance, $\boldsymbol{r}_{ij}$, so if we apply a magnetic field perpendicularly to our lattice ($\boldsymbol{B} = B\hat{z}$), we will get an isotropic repulsive potential $U = \frac{\mu_0 m^2}{4\pi r_{ij}^3}$ for equally induced moments, $m = m_i = m_j$, given that all particles are confined to the x,y-plane [2]. This repulsive potential forces the particles to maximize their distance, and in the range of values of the applied magnetic field that we are using in our study, particles are able to cross the central hill but never escape from the gravitational trap.

Then, the objective of this work is to study the evolution of a colloidal ice system with an initial random distribution of the particles in the traps, for different values of applied magnetic field, temperature and cut-off distance of dipolar interactions. To do so, we will measure the topological charge q at each vertex and see if the system follows the ice rule; or in other words, how the system reaches the ground state (where vertex's have a zero topological charge).

II. SIMULATION METHODS

We are performing numerical simulations using the "icenumerics" package [4] based on a modified version of LAAMPS to be able to run Brownian dynamics. Under these conditions, particles are assumed to be immersed in a high Reynolds number fluid, so a drag force proportional to the velocity is included in the equation of motion and the inertial term can be neglected as it is much smaller. Particles are also subjected to unpredictable random forces from the fluid, given by a Langevin term ξ, such that $\langle\xi\rangle = 0$ and $\langle\xi(t)\xi(t')\rangle = 2\eta k_B T\delta(t - t')$, where η is the viscosity, k_B is the Boltzmann constant, T is the temperature and δ is the Dirac delta function. The equation of motion of a particle i can be written as:

$$\eta\frac{d\boldsymbol{r}_i}{dt} = \boldsymbol{F}_i^{tot} + \xi \qquad (2)$$

In a colloidal ice, the force term has two contributions: the trapping force ($\boldsymbol{F}^T$), due to the gravitational confinement within the double wells, and the interaction force ($\boldsymbol{F}^M$), $\boldsymbol{F}^{tot} = \boldsymbol{F}^T + \boldsymbol{F}^M$. The first can be described as:

$$\boldsymbol{F}^T = -kr_\perp\hat{\boldsymbol{e}}_\perp + \hat{\boldsymbol{e}}_\parallel \begin{cases} k(|r_\parallel| - d/2)\mathrm{sign}(\mathrm{r}_\parallel) & : r_\parallel < d/2 \\ h(1 - 4r_\parallel^2/d^2) & : r_\parallel > d/2 \end{cases} \qquad (3)$$

where $r_\parallel$ is the component parallel to the direction of the trap, and $r_\perp$ is the perpendicular component, $\hat{\boldsymbol{e}}_\perp$ is the unit vector in the direction of the trap, $\hat{\boldsymbol{e}}_\parallel$ is a vector pointing away from the line that joins both stable points, k is the trap stiffness, d is the distance between centers and h is the stiffness of the central hill [4], shown in FIG. 3. On the other hand, the interaction force is given by:

$$\boldsymbol{F}_i^M = \sum_j \frac{3\mu_0 m^2}{2\pi|\boldsymbol{r}_{ij}|^4}\boldsymbol{r}_{ij} \qquad (4)$$

where $\boldsymbol{m}$ is the induced magnetic moment, μ_0 is the permeability of the medium and $\boldsymbol{r}_{ij}$ is the vector that goes from the particle i to the particle j [2].

A. Simulation parameters

We are simulating a square lattice of 50×50 particles with closed boundary conditions, and a separation distance of $30\mu m$ between the centers of the traps. The particles are defined with a radius of 5.15μm, susceptibility of $\chi = 0.0576$, a diffusion constant of $0.125\mu\mathrm{m}^2\mathrm{s}^{-1}$ and a density of $\rho = 1000\mathrm{kgm}^{-3}$. Also, the traps are defined with a stiffness $k = 6 \cdot 10^{-4}\mathrm{pNnm}^{-1}$, a stiffness of the central hill $h = 80pN \cdot nm$ and a distance between centers of $d = 10\mu$m. Then, to have enough statistical samples, we have run five separate simulations with unique initial particle positions for each value of the applied field, temperature and cut-off distance in order to minimize the errors. The reference values of the variables are $B = 15mT$, $T = 300K$ and $\Xi = 200\mu m$, and the simulations are executed for a total time of 500s with a ramp for the applied field during 250s until it reaches the maximum value.

III. RESULTS

A. Defect lines and ground state

If we suddenly apply a strong magnetic field to the initial random distribution of particles, the system will not reach immediately the ground state. Instead, the strong dipolar interactions between the particles rapidly force to minimize the interaction energy at a vertex, and the system can easily be trapped in a metastable state [2]. Consequently, the lattice will organise in regions that follow the ice rule and that are separated by domain walls in the form of defect lines. Once the defect lines are created they remain practically frozen in place since it is very energetically demanding to remove them as all the spins of an entire region would have to flip [2].

In the simulation we want to avoid the presence of the defect lines, so to reach the ground state of the system we will apply a slow ramp in the magnetic field amplitude which begins from 0 mT, it reaches the target value in a certain time interval and then the field remains constant until the end of the simulation (FIG. 3). In this way, the interactions between the particles will be weaker at the beginning, being easier for them to rearrange due to small thermal fluctuations in order to minimize their interaction energy and avoid metastable states, reaching the true ground state.

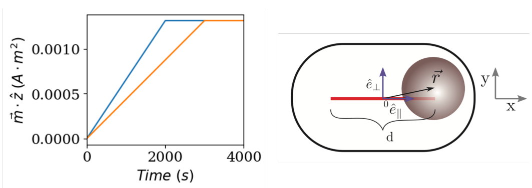

FIG. 3: ***Left*** **:**Time dependent magnetic moment, which is proportional to the applied magnetic field **B**. We can see two ramped fields corresponding to those applied in the simulations of FIG. 4 (blue) and FIG. 5 (orange). ***Right*** **:** Representation of a colloidal particle inside the trap defined in Eq.(3). Image reproduced from Ref.[5].

As shown in FIG. 4, we find that avoiding the formation of defect lines was not simple, since steep slopes in the field ramp can still induce the formation of the grain boundaries. To reach a true ground state, where all vertices of the lattice follow the two-in two-out ice rules, we had to run a simulation with a total time of 4000s and a ramped field of duration 3000s with a maximum amplitude of 15mT (FIG. 5). Moreover, one can observe in FIG. 4 and FIG. 5 that in the borders of the lattices the topological charges of the vertices are different to zero due to the fact that at the boundaries each vertex has only three spins around them and the coordination

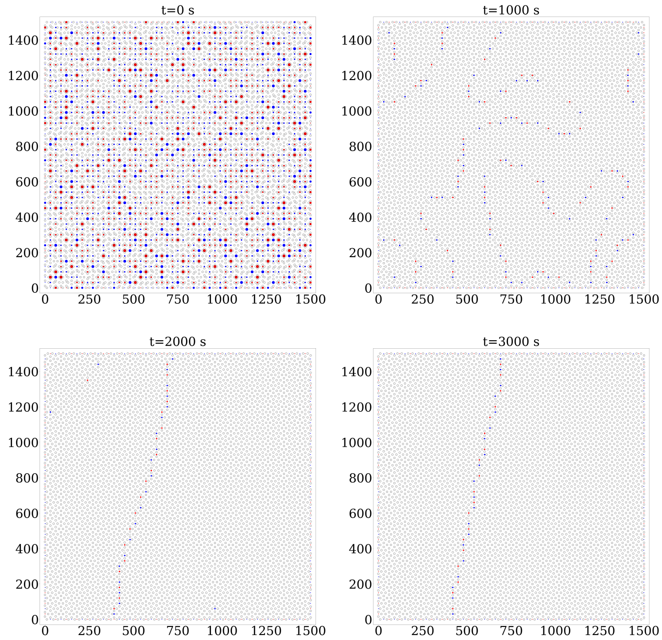

FIG. 4: Map of the topological charges associated to the lattice vertices. Blue dots represent a negative charge while red dots represent a positive charge. The total time in this simulation was 3000s and we applied a ramped field for 2000s up to 15mT. In the first map it's easy to see the random distribution of the topological charge while in the next frames we see the emergence of diverse regions separated by defect lines until the two very distinguished regions are formed in the last frame.

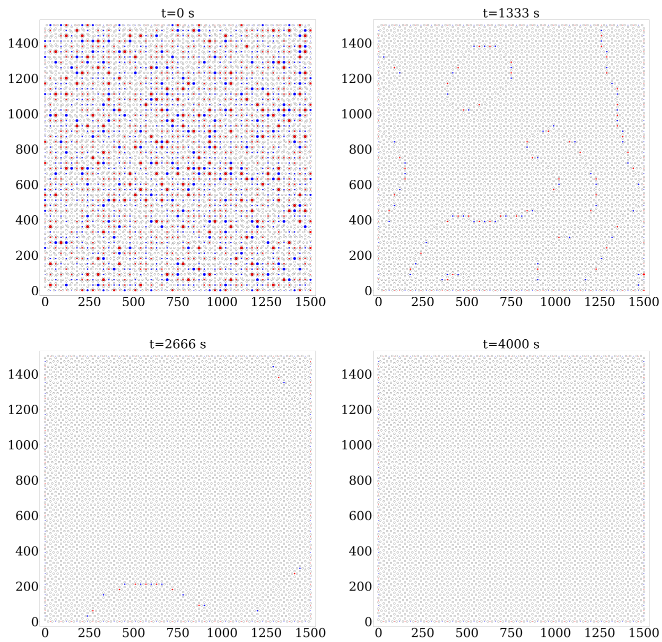

FIG. 5: Images showing the evolution of a colloidal ice where all defects disappear because the applied field ramp is larger. The last frame illustrates a perfect ground state where each vertex of the lattice follows the ice rule.

number changes. We choose to carry out the analysis on $z = 4$, ignoring $z = 3$ vertices in the future sections.

B. Magnetic field

The dipole-dipole interaction of the particles strongly depends on the applied magnetic field B, as it is shown in Eq. (1), so it is convenient to analyze the behaviour of the system when we modify this parameter. For this reason, we will study the evolution of the system for three different values of the applied magnetic field: $5mT$, $15mT$ and $25mT$. In particular, to explore the behavior of the colloidal ice, we have measured the time evolution of the average population of the different topological charges. Thus, the system will reach the ground state when the population of $q = 0$ is near to 1, while if the fraction of vertices with $|q| = 2$ and $|q| = 4$ have a non-zero value, this will imply the presence of defects in the lattice.

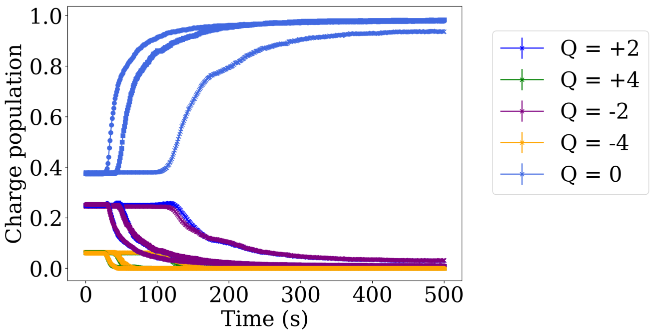

FIG. 6: Time evolution of the population of the topological charges for the three different values of the applied magnetic field; circles indicate the results for a maximum field of 25mT, squares for 15mT and crosses for 5mT. We can note that for lower field strengths the response is delayed to longer times.

In FIG. 6 I show the fraction of vertices versus time obtained from numerical simulations at the three field amplitudes. All simulations start with similar initial random conditions. These conditions are chosen such that there are 6 configurations that have $q = 0$, with a probability of $6/16 = 0.375$, 4 configurations that have $q = -2$, with probability $4/16 = 0.25$ (the same for $q = +2$) and 1 configuration for $q = -4$, with probability $1/16 = 0.0625$ (same case for $q = +4$). For short time scales, in all cases the charge populations remain constant as the interactions are too weak to modify the positions of the particles. Due to this, we can suppose that there is a threshold applied field for which the interactions begin to be strong enough to induce particle switching within the double wells and thus change the orientation of the associated pseudo-spins. We can estimate this threshold field to be of the order $B_{th} = 2.1 \pm 0.3$mT. It is also clear that the smaller the maximum field of the simulation, the longer it will take to reach this threshold field. Also, for stronger fields, the system reaches its equilibrium state faster. In all cases, we find that increasing the interaction strength induce a corresponding growth of the ice rule vertices, $q = 0$, which dominate over the other charges. Indeed vertices with $q = \pm 4$ quickly go to 0 while $q = \pm 2$ populations remain in a minimal percentage. From this we can deduce the presence of defect lines of charge $q = \pm 2$. As expected, by raising the maximum applied field value, we find that the system reaches faster the GS. In contrast, for $B = 5$mT the $q = \pm 2$ topological charges do not disappear totally, sign that the system is in a metastable state with the presence of domain walls.

C. Interaction length

I have explored next the effect of varying the cut-off distance of the dipolar interactions between the particles on the time evolution of the topological charge populations. To do this, I have limited the interaction length Ξ to three different values: 35μm (nearest neighbors), 200μm and 500μm, which is the maximum length due to the size of the lattice.

While one could expect that changing the range of the interaction potential could affect the way the system reaches the ground state, the results shown in FIG. 7 demonstrate the opposite. The system manifests practically the same behavior for the three cut-off distance. This can be explained by the shape of the isotropic potential in Eq. (1), which depends on the distance between particles in an algebraic way $1/r^3$. Thus, the nearest-neighbor interactions dominate and considering long-cut-off distances, i.e. next nearest-neighbor etc.. do not have an important effect on the dynamics of the system. In fact, we can conclude that particles mainly only interact with their nearest neighbors.

D. Thermal fluctuations

In the equation of motion (Eq. (2)) the colloidal particles are subjected to thermal fluctuations, so we want to analyze the effect of temperature on the behavior of the system. To do so, we will modify the temperature of the system and study the time evolution of the populations of topological charges for three values: 273K (freezing point of the water), 300K (approximately the room temperature) and $353K$ (near the boiling point of the water).

The results in FIG. 8 manifest that the system is unaffected to changes in the temperature and this means that the thermal fluctuations are not strong enough to allow the particles to switch within the double wells. Possibly, to see the effect of these fluctuations we would need to reduce the size of the particles or either use a smaller hill in the traps.

IV. CONCLUSIONS

In this work I have used numerical simulations to investigate a geometrically frustrated colloidal ice, where particles were confined along a square lattice of double wells, and I have studied how their interactions affect the dynamics of the system and its possible equilibrium

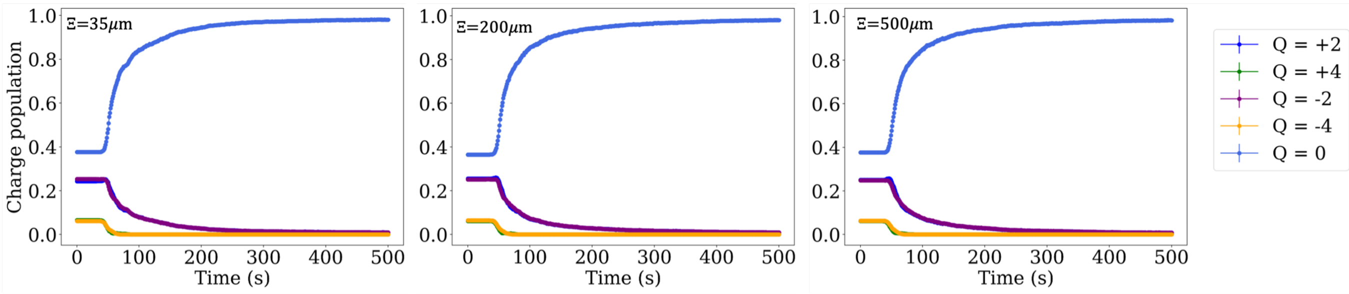

FIG. 7: Time evolution of the population of the topological charge for the three values of the cut-off distance ($35\mu m$, $200\mu m$ and $500\mu m$ respectively). In the different simulations we can prove that the system reaches the ground state because the population of charge $q = 0$ tends to 1 while the others tend to 0.

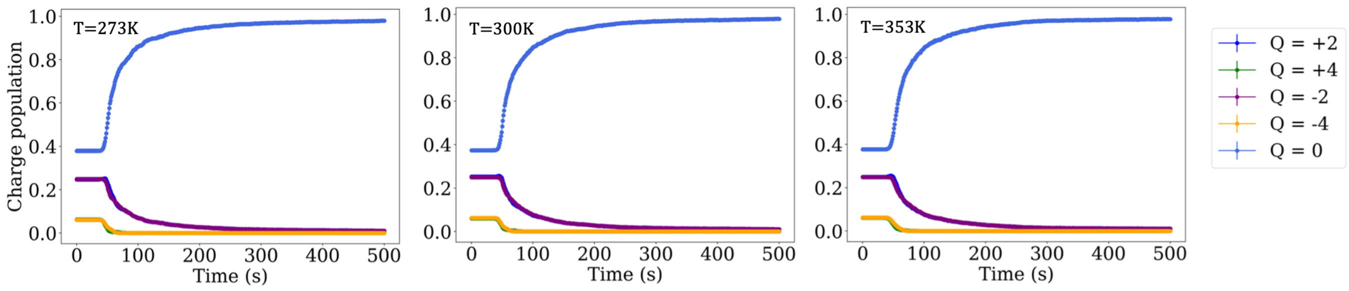

FIG. 8: Time evolution of the population of the topological charges for the three values of the thermodynamic temperature ($273K$, $300K$ and $353K$ respectively).

states. First of all, I have seen the formation of defects in the lattice when we suddenly applied an intense magnetic field, and for that reason it was necessary to apply a time dependent field with a soft slope in order to avoid metastable states and reach the ground state of the system. Since the colloidal particles used can be magnetized via application of a magnetic field and interact due to the dipole-dipole forces, I have analyzed the behavior of the system for different values of the applied field. I have found that stronger the field applied, less time will take for the system to reach its ground state. In contrast, for low intensities of the magnetic field, the system takes significantly more time to reach the equilibrium and it does it with a higher number of defects. Secondly, I have evaluated the range of these dipole interactions and I found that it decays very fast due to the nature of the interactions potential ($U \propto 1/r^3$). This shows that the colloid particles in our system are mainly influenced at the nearest neighbor level. It should be noted that the number of interactions may increase if we reduce the distance between traps because particles would be closer to each others.

Finally, I explored the effect of thermal fluctuations to see whether they are relevant to the dynamics of the system. Thus, I performed simulations for different values of the temperature and I discovered that the system evolves in the same way for all of them, indicating that thermal fluctuations are insignificant as they are too weak to allow the particles to overcome the central hill of the traps.

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