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Self-assembly of magnetic spheres in two dimensions: The relevance of onion-like structures

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Abstract – The self-assembly in two dimensions of spherical magnets is addressed theoretically. Minimal energy structures are obtained by optimization procedures as well as Monte Carlo computer simulations. For a small number of constitutive magnets $N \leq 17$, ring-like structures are found to be stable. In the regime of larger $N \geq 18$, the magnets form touching concentric rings that are reminiscent of the onion-like structures. At sufficiently large N, the (edgy) shells are hexagonal where dipole moments tend to align to the edge direction. All these relevant predicted shapes are experimentally reproduced by manipulating millimetric magnets.

Introduction. – Magnetic interactions and especially assembly of magnetic objects have always intrigued the human being [1]. The usage of magnets in the everyday life and also in the industry is ubiquitous. In nanotechnology, self-assembled mixtures of magnetic nanoparticles can lead to very strong magnets [2]. In the biological world, so-called *magnetotactic bacteria* own a permanent magnetic moment and they are able to orient and move in the direction of the magnetic field [3]. Under an external magnetic field, the latter form chain-like structures [4]. In a more physical perspective, magnetic colloidal particles [5–7], that can be envisioned as mesoscopic magnets, constitute an ideal model system to mimic and understand the phase behavior in classical molecular systems.

From a theoretical viewpoint, understanding magnetic self-assembly originating from dipolar interactions is very challenging due to the long-range and strong anisotropy involved there. The pioneering theoretical work of Jacobs and Bean [8] and later that of de Gennes and Pincus [9] shed some light on the structure shape of self-assembled spherical magnets. More recently, microstructures of dipolar fluids have been thoroughly studied by computer simulations [10,11] and a key feature is the formation of chains at *finite* temperature. The relevance of ring formations, confirmed by simulations, was advocated by Wen *et al.* [12] in magnetic microspheres and by Prokopieva *et al.* [13] in ferrofluid monolayers. In close connection to our system of interest, Vella *et al.* [14] looked at the mechanical properties of assemblies (chains, rings, and chiral cylinders) of ferromagnetic spheres. Vandewalle and Dorbolo observed a monopole-like field around V-shape junctions[1] of magnetic chains [17]. Schönke *et al.* reported an infinitely degenerate ground state for a cubic dipole cluster [18]. In previous publications [19–21], the self-assembly at zero temperature of magnetic spheres in three dimensions (3D) have been investigated. The formation of stacked rings leading to tubular structures was the major finding [19].

In this letter, we predict the ground-state microstructures of spherical magnets as a function of the number of constitutive magnets N in two dimensions (2D). Besides, commercial millimeter-sized magnets (commonly called *Buckyballs* or *Neodyme spheres*), see inset in fig. 1, are employed to exemplify some calculated ground-state structures.

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[1] Note that the existence and importance of similar Y-junctions in dipolar systems have been pioneered by Tlusty and Safran [15] and investigated later by computer simulations by Ilg and Del Gado [16].

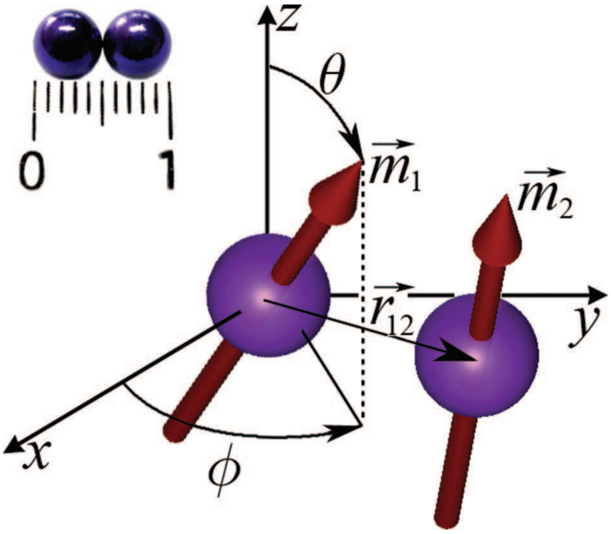

Fig. 1: (Colour on-line) Scheme of two interacting spherical magnets. For commodity one magnet is placed at the origin so that $\vec{r}_1 = 0$. The polar and azimuthal angles (θ, ϕ) are explicitly shown for $\vec{m}_1$. The inset (top left corner) of a 1 ruler centimeter exemplifies the millimeter-sized magnets utilized in our experiments.

Model. – The length scale of the system is given by the diameter d of the spherical magnet, see fig. 1, and its dipole moment strength is $m = |\vec{m}|$. The potential of interaction $U(\vec{r}_{12})$ between two such magnets whose centers are located at $\vec{r}_1 = (x_1, y_1)$ and $\vec{r}_2 = (x_2, y_2)$, see fig. 1, can be written as

$$U(\vec{r}_{12}) = C\frac{1}{r_{12}^3}\left[\vec{m}_1 \cdot \vec{m}_2 - 3\frac{(\vec{m}_1 \cdot \vec{r}_{12})(\vec{m}_2 \cdot \vec{r}_{12})}{r_{12}^2}\right] \qquad (1)$$

for $r_{12} \geq d$ or infinite otherwise, where C represents a constant that depends on the intervening medium, and $r_{12} = |\vec{r}_{12}| = |\vec{r}_2 - \vec{r}_1|$. Like in [19], the energy scale is set by $U_{\uparrow\uparrow} \equiv \frac{Cm^2}{d^3}$ corresponding to the repulsive potential value for two parallel dipoles at contact standing side by side as clearly suggested by the notation. Thereby the reduced potential energy of interaction per magnet, u_N, for an assembly of N magnetic spheres reads

$$u_N = \frac{1}{N}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{U(\vec{r}_{ij})}{U_{\uparrow\uparrow}} \qquad (r_{ij} \geq d). \qquad (2)$$

For the particular head-to-tail configuration (*i.e.*, $\rightarrow\rightarrow$) we get $u_2 = -2$.

Method. – It is specifically the function appearing in eq. (2) that has to be minimized by carefully taking into account the non-overlapping conditions. Note that upon searching the minimal energy, four variables per magnet are involved, see also fig. 1: two Cartesian coordinates (x, y) for the center, and two angular parameters (θ, ϕ) for the unit vector defining the direction of the dipole moment. Two fully different numerical routes were carried out to calculate the energy minimum of the system: i) standard minimization routines (*e.g.* penalty method [22]) and ii) Monte Carlo (MC) simulations [23]. In the latter case, a gentle quench from finite to zero temperature is applied so as to avoid an early trapping in local minima. Single-particle moves have been performed consisting of i) translational trial displacements for the particle centers as well as ii) angular ones for the dipoles. When zero temperature is attained, only trial moves leading to lower energies are accepted. In order to increase the chance of finding the global minimum, typically 10^3 to 10^4 starting configurations were considered. The winning structure is then the one possessing the lowest energy.

Results. – Our main result can be found in fig. 2 where the reduced energy u_N as a function of N is depicted. Typical relevant structures are also provided there, so that fig. 2 serves as a phase diagram as well. We are going to analyze and discuss this energy-phase diagram.

As a general preliminary remark, we want to point out that the minimization procedure always finds dipole moments lying in the same plane containing the particles. This feature can be easily demonstrated by inspecting the pair potential (1). Clearly, we have to deal with magnets living in the (x, y)-plane as sketched in fig. 1, with dipole moments of the form $\vec{m}_i = (m_{ix}, m_{iy}, m_{iz})$ verifying the constraints $m^2 = m_{ix}^2 + m_{iy}^2 + m_{iz}^2$ $(i = 1, \ldots, N)$. Thereby, we are asked to minimize the pair potential $U(\vec{r}_{12})$ with respect to m_{1z} and m_{2z} taking into account the constraint functions $\Psi_1 = m_{1x}^2 + m_{1y}^2 + m_{1z}^2 - m^2 = 0$ and $\Psi_2 = m_{2x}^2 + m_{2y}^2 + m_{2z}^2 - m^2 = 0$. Hence, we now consider the auxiliary constrained function

$$G = U + \lambda_1\Psi_1 + \lambda_2\Psi_2, \qquad (3)$$

where λ_1 and λ_2 stand for the Lagrange multipliers [24]. Doing so, the required conditions for minima, $\frac{\partial G}{\partial m_{1z}} = 0$ and $\frac{\partial G}{\partial m_{2z}} = 0$, straightforwardly yield $m_{1z} = m_{2z} = 0$ (see footnote [2]). As a consequence and thanks to the superposition principle, an assembly of dipole moments must always be coplanar with the flat substrate in the (2D) ground state.

In the regime of very small $N \leq 3$, short straight chains are found as ground states (not shown here) as already discussed in the literature [8,19]. Then, up to $N = 17$, rings with energy

$$u_N^{(ring)} = -\frac{1}{4}\sin^3\left(\frac{\pi}{N}\right)\sum_{k=1}^{N-1}\frac{3 + \cos\left(\frac{2\pi k}{N}\right)}{\sin^3\left(\frac{\pi k}{N}\right)} \qquad (4)$$

[2]It is a trivial task to show that the minimization of the *unconstrained* function U with respect to m_{1z} and m_{2z} leads to the very same conclusion ($m_{1z} = m_{2z} = 0$).

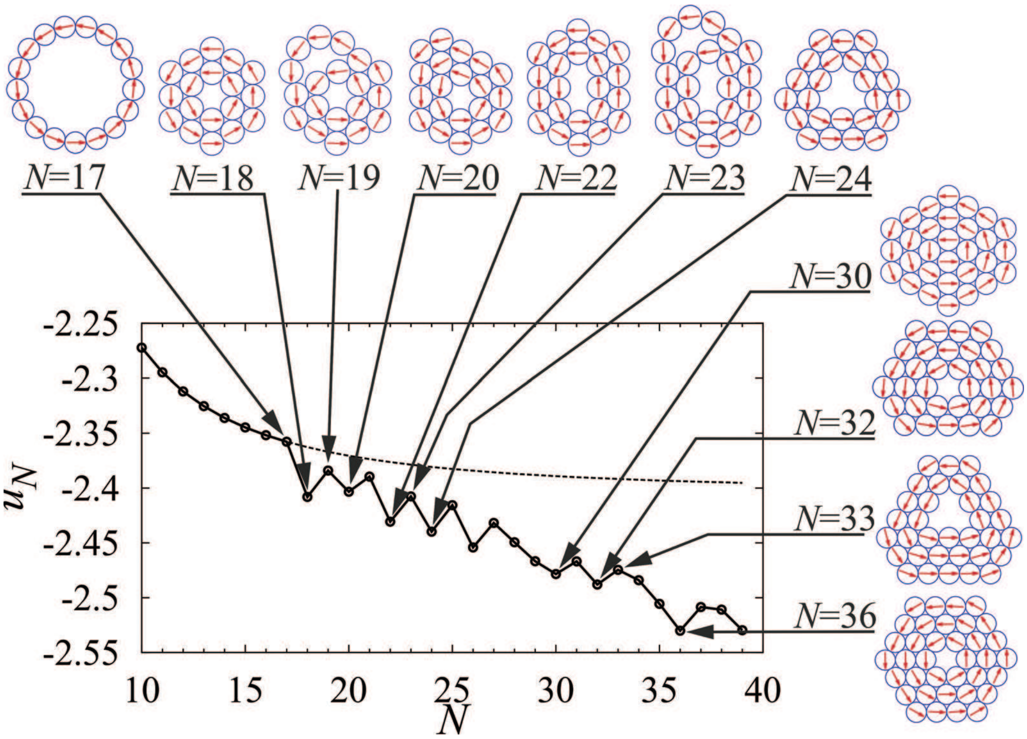

Fig. 2: (Colour on-line) Reduced energy profiles u_N as a function of the number of magnets N. Relevant microstructures are shown for certain values of N. The dashed line corresponds to the energy of an ideal ring as given by eq. (4).

are found as ground states ($4 \leq N \leq 17$). The experimental case, $N = 17$, is illustrated in fig. 3(a)[3]. This type of structure was already found and discussed for the unconfined 3D situation [19]. All the same, in 3D, rings are energetically favorable only up to $N = 13$, where stacking of rings win when $N \geq 14$ [19]. The first remarkable and crucial transition occurs at $N = 18$, where two (perfect) touching concentric *hexagonal* rings are the lowest-energy states, see fig. 2. The experimental realization of this arrangement is provided in fig. 3(b). In that situation, the microstructure significantly densifies, when compared to the single-ring situation ($N = 17$), into a two-shell onion compact structure. This feature explains the strong energy drop, see fig. 2, when passing from $N = 17$ (ring structure) to $N = 18$ (onion structure). It turns out that the regular polygonal onion-shell arrangement is a key feature in the 2D self-assembly of magnetic spheres and can be seen as a defect-free ground-state reference. As a matter of fact, all the ground-state structures found so far ($1 \leq N \leq 18$) are defect free.

The appearance of the first structural defect occurs at $N = 19$, see fig. 2. Thereby a local "buckling" of the outer shell occurs due to the frustration of being able to build concentric touching rings[4]. Interestingly, this defect is perfectly experimentally reproduced by manipulating millimetric magnetic balls, see fig. 3(c). This feature explains also the observed energy jump when passing from $N = 18$ to $N = 19$, see fig. 2, leading to a local maximum. More generally, the rough nature of the energy landscape (from $N > 19$) revealed in fig. 2 is a consequence of this kind of frustration. Two-shell structures are energetically favorable for $18 \leq N \leq 28$. Clearly, structures with voids within two shells as found for $N = 19$ exhibit local maxima, see fig. 2 with $N = 21, 23, 25$, and 27. On the other hand, two-shell structures with touching shells (not necessarily hexagonal or regular) lead to local minima, see fig. 2 with $N = 18, 20, 22, 24$ and 26. An example of experimental realization for $N = 24$ is provided in fig. 3(d).

Upon further increasing N (here $N \geq 29$) structures involving more than two shells set in. Depending on the value of N, the winning microstructure can possess more or less symmetry, as can be seen in fig. 2. For special magic numbers N_{hex} following

$$N_{hex} = 3p^2 - 3p \tag{5}$$

with p denoting the number of particles per outer edge for a perfect hexagonal shell ordering, the structures have then the highest symmetry (here $N = 36$ with $p = 4$

[3]Note that in our model we deal with point-like dipoles, whereas in the experimental situation the magnets are millimetric. Hence, when comparing theory *vs.* experiments, one has to bear in mind that higher multipolar contributions are neglected, which is a good approximation for the level of comparison (*i.e.*, particle arrangement) in the present work. Dipoles with finite extension have been studied by molecular dynamics in the context of colloidal suspensions in the past, see, *e.g.*, Blaak *et al.* [25].

[4]From a purely geometric point of view, a compact defect-free structure could be obtained with $N = 19$ when filling the central void present at $N = 18$. However, introducing there a dipole in an environment of zero global magnetization is energetically unfavorable when the system is small.

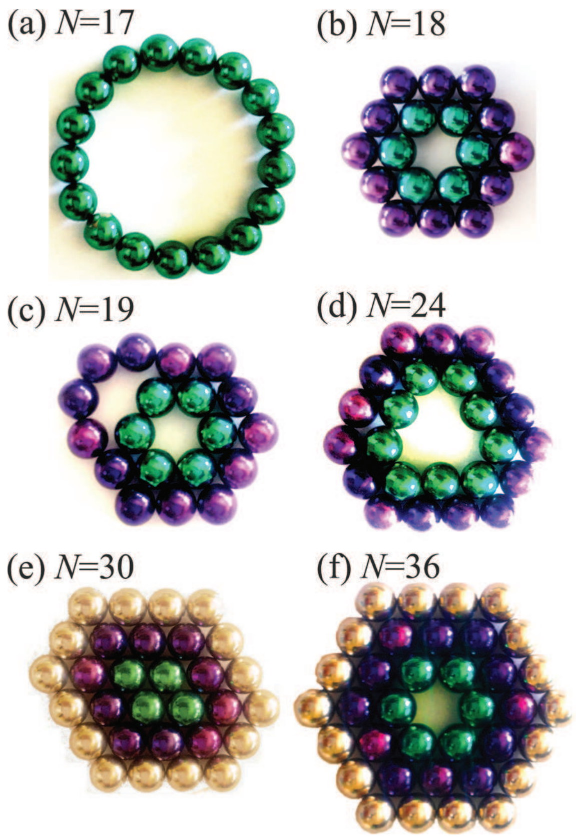

Fig. 3: (Colour on-line) Some illustrative configurations of millimetric commercial magnetic beads obtained in our experiments. The diameter of a bead is about 5 mm. (a) $N = 17$ showing a regular polygonal ring structure. (b) $N = 18$ showing the regular two-shell hexagonal structure. (c) $N = 19$ showing the defect where a void appears between two shells. (d) $N = 24$ showing a regular triangle-based two-shell structure. (e) $N = 30$ showing a regular lozenge-based two-shell structure. (f) $N = 36$ showing the regular three-shell hexagonal structure.

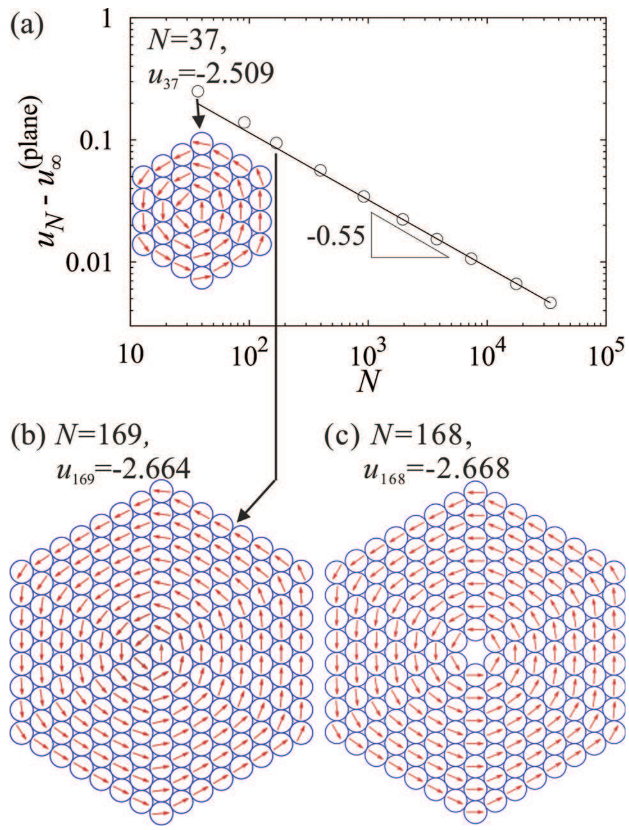

Fig. 4: (Colour on-line) (a) Relative reduced energy profiles $u_N - u_\infty^{(plane)}$ as a function of the number of magnets N for hexagonally shaped onions with filled cores ($N = 3p^2 - 3p + 1$, compare with eq. (5)). For convenience, only some values of N are shown (circles) covering roughly three decades. The full line represents a power law of the form $N^{-0.55}$ which corresponds to the best fit. The microstructure for $N = 37$ is provided, to be compared with that for $N = 36$ in fig. 2. Comparative microstructures for a larger number of shells are depicted for (b) $N = 169$ and (c) $N = 168$

in eq. (5)) leading to a deep local minimum, see fig. 2[5]. Comparative experimental examples of high symmetrical three-shell ordering are provided for $N = 30$ and $N = 36$ in fig. 3(e) and (f), respectively.

To gain further understanding of the ordering at larger N we will solely consider perfect hexagonal shells. Typically, two scenarios emerge:

– There is no void in the core so that the hexagonal basis is filled with one particle in its center as illustrated for $N = 37$ and $N = 169$ in fig. 4(a) and (b), respectively.

– There is a void in the core corresponding exactly to one missing particle as already found for $N = 18$ and $N = 36$, see fig. 2. The case of larger N is illustrated for $N = 168$ in fig. 4(c).

It is insightful to introduce the limit of an infinite planar triangular lattice with parallel dipole moments corresponding to $u_\infty^{(plane)} \simeq -2.759$ [19]. Thereby, the profile of $u_N - u_\infty^{(plane)}$ for several decades is depicted in fig. 4 for hexagonally shaped onions with filled cores. For $N = 37$, there is an energy deviation of about 10% from the infinite case, see fig. 4(a). This is essentially due to finite-size effects that are still non-negligible there. A closer visual inspection of the corresponding microstructure, see fig. 4(a), reveals a pretty strong asymmetry in the dipole arrangement within the first shell surrounding the filled core. This asymmetry gradually vanishes upon getting further away from the core, see fig. 4(a). When N is large enough, already with $N = 169$, the energy deviation from the infinite case drops to about 4%. The situation with perfectly aligned dipole moments within parallel edges is virtually recovered from four shells away from the core, see fig. 4(b). The situation is qualitatively the same with an empty core ($N = 168$), see fig. 4(c) leading to nearly

[5]The very same high symmetry is evidently also vivid for two-shell structures at $N = 18$ with $p = 3$ in eq. (5).

the same reduced energy $u_{168} = -2.668$ as that obtained for a filled core $u_{169} = -2.664$.

Concluding remarks. – In summary, we have investigated the self-assembly of N magnetic spheres in two dimensions. The essential finding is the formation of shells, reminiscent of onion ones, that possess more or less symmetry depending on the value of N. A general result is the tendency to produce zero or small global magnetization $\vec{M} \equiv \frac{1}{N}\sum_i \vec{m}_i$ owing to dipole moments forming (edgy) vortices. This feature at finite N is consistent with the idea that the magnetic energy density w is proportional to the square of the local generated magnetic field ($w \propto B^2$) anywhere in the space, and that in the far-field limit $B \propto M$.

In the regime of a small number of magnets $4 \leq N \leq 18$, the *single* ring (regular polygon) is the lowest-energy structure, as also found in the unconfined 3D case but for $4 \leq N \leq 13$ [19]. Deep local minima are then obtained for hexagonally shaped onions structures in the regime of larger N.

In contrast to the unconfined 3D situation where empty tubes are energetically favorable for moderate N, it turns out that only dense structures are stable in 2D for $N \geq 18$. All these predicted structure classes are reproduced experimentally with millimetric magnetic balls as demonstrated in this paper. An interesting future study will deal with the effect of an external applied magnetic field where the role of chain aggregation is crucial [26].

* * *

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