Self-Assembly of Magnetic Spheres in Strong Homogeneous Magnetic Field

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The self-assembly in two dimensions of spherical magnets in strong magnetic field is addressed theoretically. It is shown that the attraction and assembly of parallel magnetic chains is the result of a delicate interplay of dipole-dipole interactions and short ranged excluded volume correlations. Minimal energy structures are obtained by numerical optimization procedure as well as analytical considerations. For a small number of constitutive magnets \( N_{\text{tot}} \leq 26 \), a straight chain is found to be stable. In the regime of larger \( N_{\text{tot}} \geq 27 \), the magnets form two touching chains with equally long tails at both ends. We succeed to identify the transition from two to three touching chains at \( N_{\text{tot}} = 129 \).

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I. INTRODUCTION

There are several reasons for strong and growing interest in self-assembled structures of dipolar particles (i.e., with electric or magnetic dipoles). On the technological side, such systems have enormous potential applications. For instance, manufacturing of novel optical and stimuli-responsive materials is based on self-assembly of magnetic particles [1, 2]. On the other hand, dipolar particles and the resulting phases can be well tuned by imposing an external field [3, 4]. Assemblies of magnetic particles are known to produce a plethora of one-, two-, and three dimensional objects (e.g., chains, rings, and even tubes) [5, 6]. From the perspective of biophysics, magnetic particles can be regarded as a model system for probing the polar organization of microtubules [7] or generating spontaneous helical superstructures [8] reminiscent of DNA molecules.

By essence, the dipole-dipole driving force for self-assembly is long range and highly anisotropic (i.e., non-central pair potential) [10, 11] and therefore represents a formidable theoretical challenge. In this spirit, the pioneering theoretical work of Jacobs and Beans [12] and later that of de Gennes and Pincus [13] about the microstructure of self-assembled (spherical) magnets shed some light on the ordering mechanisms. More recently, microstructures of dipolar fluids have been thoroughly studied by computer simulations [14, 16] and in experiments [17]. There, an important common feature is the formation of chains [14, 16] and possibly in presence of an external magnetic field [15, 17]. With all that being said, only recently, the ground state structures of magnetic spheres without external magnetic field have been properly addressed in three dimensions [6, 18, 19] as well as in two dimensions [7].

The goal of the present contribution is to tackle the fascinating problem of self-assembly of magnets under strong magnetic field in a physically simple and transparent frame-work. We explore (effective) interactions and assemblies of magnetic beads with parallel dipoles (e.g., as obtained by a strong external magnetic field) and confined in two dimensions (e.g., by gravity). We utilize two fully different routes to calculate the energy minimum of the system: (i) genetic algorithm and (ii) direct calculation and comparison of the energy of different configurations. The paper is organized as follows: In Sec. II we expose the magnetic chains Hamiltonian. Sec. III is devoted to the analytical results dealing with the two-chain state. Phase diagram of self-assembled magnets obtained by numerical genetic algorithm is discussed in Sec. IV. Concluding remarks are provided in Sec. V.

II. MODEL

A. Pair interaction potential

We begin by considering two magnetic hard spheres of diameter \( d \) separated by a distance \( r_{12} = |\vec{r}_2 - \vec{r}_1| > d \), where \( \vec{r}_1 \) and \( \vec{r}_2 \) represent the position vectors of the centers of particle 1 and particle 2, respectively. These spherical magnets being also characterized by a magnetic moment \( (\vec{m}_1, \vec{m}_2) \), the pair potential energy is dictated by:

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

where \( C \) is a constant that depends on the intervening medium (eg, for vacuum \( C = \frac{4 \pi \mu_0}{3} \) with \( \mu_0 \) being the vacuum permeability).

The approach we adopt in this work is based on the calculation of the magnetic energy of various configurations of spheres in externally imposed magnetic field \( \vec{B} = B \vec{e}_x \) aligned with \( x \)-axis. We assume that the external magnetic field is strong, i.e. \( B \gg m_C^{-1} \) (with \( m := |\vec{m}_1| = |\vec{m}_2| \)), so that all dipole moments in the system are aligned with \( \vec{B} \) and hence parallel to the \( x \)-axis, i.e. \( \vec{m} = m \vec{e}_x \). In this limit of strong field, the pair potential \([1]\) becomes

\[
U(\vec{r}_{12}) = C \frac{m^2}{r_{12}^3} \left[ 1 - 3 \left( \frac{x_2 - x_1}{r_{12}} \right)^2 \right]. \tag{2}
\]
B. Chains Hamiltonian

It is convenient to introduce the energy scale defined by

\[ U_{\uparrow\uparrow} = \frac{C_m a^2}{d} \]

that physically represents the repulsive potential value for two parallel dipoles at contact standing side by side as clearly suggested by the notation. The dipoles attract if placed with head-to-tail (i.e., \( \rightarrow \rightarrow \)). The latter promotes formation of one dimensional chains consisting of many dipoles (i.e., \( \rightarrow \rightarrow \rightarrow \)). The reduced total potential energy of interaction of a system consisting of two chains made up of \( N_1 \) and \( N_2 \) particles, \( U_{N_1N_2}^{\text{tot}} \), can be written as

\[ U_{N_1N_2}^{\text{tot}} = \frac{1}{2} \sum_{i\neq j=1}^{N_1+N_2} \frac{U(r_{ij})}{U_{\uparrow\uparrow}} (r_{ij} \geq d). \quad (3) \]

The sum in Eq. (3) can be separated into three terms,

\[ U_{N_1N_2}^{\text{tot}} = U_{N_1N_2}^{\text{ic}} + U_{N_1N_2}^{\text{cc}} + U_{N_1N_2}^{\text{xc}}, \quad (4) \]

where \( U_{N_1N_2}^{\text{ic}} \) are the reduced intra-chain contributions to the total energy, whereas \( U_{N_1N_2}^{\text{cc}} \) is the inter-chain (or cross chain) contribution to the total energy.

More explicitly, the reduced intra-chain energy \( U_N^{\text{ic}} \) is given by

\[ U_N^{\text{ic}} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{U(r_{ij})}{U_{\uparrow\uparrow}} (r_{ij} \geq d) \quad (5) \]

respecting the non-overlapping conditions. Thereby, the expression for \( U_N^{\text{ic}} \) in reduced units is merely given by

\[ U_N^{\text{ic}} = - \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{2}{(j-i)^2} = -2 \sum_{i=1}^{N-1} \frac{N-i}{3}. \quad (6) \]

This always negative energy in Eq. (6) can be seen as the cohesion energy of a magnetic chain. On the other hand, the inter-chain term \( U_N^{\text{cc}} \) in Eq. (4) can be either positive or negative depending on the relative x-shift of the two chains. Assume chain 1 has its first bead at \( x_1^{(1)} \) so that its last one is at \( x_1^{(N_1)} = x_1^{(1)} + N_1 d \). Given the symmetry of the system, chain 2 position is then fully specified by the position of its first bead \( x_2^{(1)} = x_1^{(1)} + \delta_x d \), with \( \delta_x \) representing the relative x-shift of the two chains. The relative position of two beads \( i \) and \( j \) belonging to chain 1 and chain 2, respectively, can be written as \( r_{ij}/d = (j-i+\delta_x,\delta_y) \), where \( \delta_y \) is the relative (reduced) y-position of the two chains. We then arrive at the simple expression for cross chain interaction energy

\[ U_{N_1N_2}^{\text{cc}}(\delta_x,\delta_y) = \sum_{i=1}^{N_2} \sum_{j=1}^{N_1} \left\{ \frac{1}{(j-i+\delta_x)^2 + \delta_y^2} - \frac{3(j-i+\delta_x)^2}{[(j-i+\delta_x)^2 + \delta_y^2]^2} \right\}. \quad (7) \]

![FIG. 1: (a) Reduced cross energy profile of a single magnet interacting with a chain made up of \( N_i \) magnetic beads. The center of the single magnet is located at a \( \delta_y \) distance from the chain and always at the x-mid-height of the latter. (b) Sketch at contact for \( N_c = 2, 4, 6 \) where \( \delta_y = \sqrt{3}/2 \).](image)

The effective force between these two chains in the direction perpendicular to the external magnetic field is then given by

\[ F_y^{\text{cc}} = -\nabla_{\delta_y} U_{N_1N_2}^{\text{cc}}(\delta_x,\delta_y). \]

Hence, when talking about attraction vs repulsion, it is the sign of that effective force that will matter.

III. INTERACTION OF TWO CHAINS

A. Chain-dipole interaction

It is instructive to first consider the interaction between a chain and a single magnet. Thereby, the most elementary situation consists of a single magnet (i.e., \( N_1 = 1 \)) interacting with a dimer (i.e., \( N_2 = 2 \)). An important configuration is that corresponding to a triangle, see inset in Fig. (1) for \( N_c = 2 \), since this is also the local configuration of an infinite triangular lattice. Thereby, the (equilateral) triangle configuration energy is merely given by \( U_{12}^{\text{cc}}(\delta_x = 1/2, \delta_y = \sqrt{3}/2) = 1/2 \), see also Fig. 1. The positive value indicates that there is a strong energy penalty upon assembling a magnetic dimer and a single magnet together into a triangle from infinite relative separation. This feature is clearly consistent with the geometrical idea that 60° is larger than the magic angle 54.7°.
Interestingly, upon slightly separating the two objects (keeping $\delta_x = 1/2$), there is a slight increase in energy proving an effective attraction, see Fig. 1. At large separation, one recovers the behavior of two point-like dipoles leading to a typical repulsion scaling as $1/\delta_y^3$.

When increasing the chain size by the same amount on both ends, the energy at contact for a flat T-shaped configuration is significantly decreased, see Fig. 1. This is merely due to the attractive terms stemming from the interaction between the further dipoles of the chain with the single aside magnet. This energy at contact becomes asymptotically $U_{\infty}^{CC}(\delta_y = \sqrt{3}/2) \simeq -0.356$ for an infinite chain. Concomitantly, the energy barrier upon approaching a magnet from infinity vanishes when the chain gets very large, see Fig. 1. Thus, chain size qualitatively matters, and peripheral dipoles along the chain screen the repulsion between the aside magnet and its first neighbours. At small $\delta_y$-separation, deep minima are attained (see Fig. 1) showing that the interaction strength with satellite dipoles overcompensates that with first neighbours.

B. Two-chain state

1. Like sized chains

We now would like to provide a more quantitative analysis of interaction of two equally long chains. Taking advantage of the symmetry the cross energy expression with respect to indices when $N_1 = N_2 = N$ in Eq. (7), we find:

$$U_{NN}^{CC}(\delta_x, \delta_y) = \sum_{i=-N+1}^{N-1} (N - |i|) \left\{ \frac{1}{(i + \delta_x)^2 + (\delta_y/2)^2} ight. \\
\left. - \frac{3(i + \delta_x)^2}{(i + \delta_x)^2 + (\delta_y/2)^2} \right\}$$  (8)

The profiles of the interaction potential of two chains with $N = 20$ particles can be found in Fig. 2. In this scenario, we want to illustrate the crucial effect of positional lateral correlations. As expected, the strongest repulsion occurs for chains standing exactly face to face with zero lateral shift (i.e., $\delta_x = 0$), see Fig. 2. A small shift amount, here $\delta_x = 1/2$ (see Fig. 2), drastically changes the situation where now effective attraction takes place at short transverse $\delta_y$-separation. Differently said, self-assembly with $\delta_x = 1/2$ is now favored where the lowest energy is obtained at contact with local high packing. Typically, see Fig. 2. Upon increasing the relative lateral shift $\delta_x$ between the chains, a similar behavior is observed. More specifically, shifted chains with beads standing exactly face to face (i.e., for $\delta_x$ assuming integer values, say $n$) always lead to higher energy $\delta_y$-profiles than with $\delta_x = n + 1/2$, especially near contact, see Fig. 2(b). Besides, the near field repulsion observed for integer values of $\delta_x$ switches to attraction if particles of one chain are in the x-middle-point positions of the other chain ones (i.e., for $\delta_x = 0.5, 5.5,$ and $12.5$), see Fig. 2. In the far field limit (i.e., $\delta_y/N \gg 1$), magnetic chains should behave as super dipoles, i.e., point-like dipoles with strength $Nm$. Indeed, at sufficiently large chain-chain distance repulsion sets in with a $1/\delta_y^3$ power law dependence on distance, see inset in Fig. 2(a). The point where near field attraction switches into repulsion can be understood as a crossover between far and near field behavior. As a matter of fact, lateral correlations between discrete finite magnets are essential to promote effective attraction between facing chains within distances that are of the order of the chain itself (i.e., $\delta_y/N \lesssim 1$).

To isolate the effects of lateral displacement along the chain axis (or equivalently the external magnetic field), we consider two touching equally long chains exhibiting locally a densely packed triangular structure, see microstructures in Fig. 3. It is useful in this context to introduce integer values of displaced beads via the relation $\delta_x = n + 1/2$. Here the value of $n$ tells about the tail length, i.e., the number of beads of one chain

![FIG. 2: (a) Interchain interaction energy (per particle) profile as a function of the reduced transverse chain-chain $\delta_y$-separation for different values of the lateral chain-chain reduced shift $\delta_x$. Notice the breaking in the energy-axis allowing logarithmic scale for positive and negative values. (b) Microstructures of chains at contact for different values of $\delta_x$, oriented in the magnetic field $\vec{B}$ direction.](image-url)
end that are not in contact with the other chain, see Fig. 3 for illustrative configurations with \( \delta = 0, 2, 5, 9 \). The total energy of our two assembled chains, \( U^\text{tot}_N = U^\text{NN}_N(\delta + 1/2, \sqrt{3}/2) \), can be written according to Eq. (1) as a sum of (i) twice the single chain cohesion energy \( 2U^\text{cc} \) and (ii) the cross chain energy \( U^\text{cc} \):

\[
U^\text{NN}_N(\delta + 1/2, \sqrt{3}/2) = 2U^\text{cc} + U^\text{NN}_N(\delta + 1/2, \sqrt{3}/2). \tag{9}
\]

In a similar way that Eq. (6) has been derived, regrouping of repeating terms in the double sum [see Eq. (7)] involved in \( U^\text{NN}_N(\delta + 1/2, \sqrt{3}/2) \) entering Eq. (9) leads to a simple single sum expression given by

\[
U^\text{NN}_N(\delta + 1/2, \sqrt{3}/2) = \sum_{i=-N+1}^{N-1} (N-i) \frac{1}{[(i+\delta+\frac{1}{2})^2 + \frac{3}{4}]} - \frac{3(i+\delta+\frac{1}{2})^2}{[(i+\delta+\frac{1}{2})^2 + \frac{3}{4}]} \tag{10}
\]

Profiles of the total energy per particle, \( U^\text{NN}_N(\delta)/2N \), as a function of the relative lateral displacement \( \delta \) are displayed in Fig. 3 for three chain lengths \( (N = 6, 10, 26) \). For short chains (here \( N = 6 \)) two minima are setting in, see Fig. 3. The first and lowest minimum occurs at \( \delta = 2 \). Its origin is a subtle balance between (i) a positive contribution due to first neighbor interactions and (ii) a negative contribution due to distant neighbor interactions. These two mechanisms were clearly identified in Sec. III A, see also Fig. 1. Since at \( \delta = 5 \) the chains do not overlap (only touching ends), the second observed minimum is purely a result of distant neighbour interactions, see 3. As the chain length is increased \( (N = 10, 26) \) these features persist: (i) always a lowest minima at \( \delta = 2 \) and (ii) a second minimum at chain-chain separation (i.e., \( \delta = N - 1 \)), see Fig. 3.

At this point, we would like to answer the following intriguing question: Does the particular \( \delta = 2 \) shift value always correspond to the ground state for two like sized chains? In other words, when two identical magnetic chains self-assemble in their ground state, do they always exhibit three-bead long tails at both ends? To rationalize this striking finding, we consider the following observable

\[
\Delta U^\text{ass}_{2N}(\delta) = U^\text{ass}_{2N}(\delta) - U^\text{ass}_{2N}(\delta-1) \tag{11}
\]

which is merely the energy difference of two states at \( \delta \) and \( \delta - 1 \), respectively. (24) Since the cohesion energy is unchanged at prescribed chain size \( N \), the discrete energy variation \( \Delta U^\text{ass}_{2N}(\delta) \) given by Eq. (11) reads

\[
\Delta U^\text{ass}_{2N}(\delta) = \sum_{i=-N+\delta}^{N+\delta+1} \left\{ \frac{1}{[(i+\frac{1}{2})^2 + \frac{3}{4}]} - \frac{3(i+\frac{1}{2})^2}{[(i+\frac{1}{2})^2 + \frac{3}{4}]} \right\} \tag{12}
\]

Profiles of \( \Delta U^\text{ass}_{2N}(\delta) \) are shown in Fig. 4 for finite \( N \). It clearly illustrates the behavior of \( \Delta U^\text{ass}_{2N}(\delta) \) with respect to \( \delta \) and \( N \). More specifically, for overlapping chains (i.e., \( \delta < N - 1 \)), the energy variation \( \Delta U^\text{ass}_{2N}(\delta) \) increases at given \( \delta \) with growing chain size \( N \), see Fig. 4. Moreover, \( \Delta U^\text{ass}_{2N}(\delta) \) assume positive values for \( 2 < \delta < N - 1 \). For large \( N \), the second term in Eq. (12) converges to zero, so that the behavior of \( \Delta U^\text{ass}_{2N}(\delta) \) is solely dictated by the first term. A straightforward summation leads to \( \lim_{N \to \infty} \Delta U^\text{ass}_{2N}(\delta = 2) = 0.019 < 0 \) and \( \lim_{N \to \infty} \Delta U^\text{ass}_{2N}(\delta = 3) = 0.162 < 0 \). This demonstrates that \( \delta = 2 \) is indeed the ground state of two assembled like sized chains.
2. Unlike sized chains

In case of uneven total number of particles ($2N + 1$), we pay attention to the important situation of two symmetrically placed chains with $N + \delta + 1$ and $N - \delta$ beads, see Fig. 5 for an illustration with $\delta = 2$. [22] The energy of this system denoted by $U_{2N+1}^{\text{ass}}(\delta)$ is given by

$$U_{2N+1}^{\text{ass}}(\delta) = U_{N-\delta}^{\text{lec}} + U_{N+\delta+1}^{\text{lec}} + U_{N-\delta,N+\delta+1}^{\text{rc}}(\delta + 1/2, \sqrt{3}/2), \quad (13)$$

where the cross chain term reads

$$U_{N-\delta,N+\delta+1}^{\text{rc}}(\delta + 1/2, \sqrt{3}/2) =$$

$$2 \sum_{i=0}^{N-1} \min(N - i, N - \delta) \times \left\{ \frac{1}{[(i + \frac{1}{2})^2 + \frac{3}{4} \delta^2]} - \frac{3(i + \frac{1}{2})^2}{[(i + \frac{1}{2})^2 + \frac{3}{4} \delta^2]} \right\}, \quad (14)$$

and the intra-chain terms $U_{N-\delta}^{\text{lec}}$ and $U_{N+\delta+1}^{\text{lec}}$ are specified by Eq. (6). Typical relevant profiles of $\Delta U_{2N+1}^{\text{ass}}(\delta)$ as given by Eq. (13) are shown in Fig. 4 for finite $N$. Again, the value $\delta = 2$ plays a special role in the energy minimum of assembled chains, see Fig. 5. It can be emphasized that, in the regime of touching chains (i.e., when $\delta \leq N - 1$), a single minimum appears and always at $\delta = 2l$, see Fig. 5. It is interesting to notice that for a given number of total particles $2N + 1$, the two-chain structure beats energetically the single-chain one only when $N$ is large enough, see Fig. 5 [23].

In the same spirit of Eq. (11), we define the discrete energy change $\Delta U_{2N+1}^{\text{ass}}(\delta)$ upon variation of lateral displacement $\delta$

\[ \Delta U_{2N+1}^{\text{ass}}(\delta) = U_{2N+1}^{\text{ass}}(\delta) - U_{2N+1}^{\text{ass}}(\delta - 1). \]

It is a simple matter to show that this quantity reads

$$\Delta U_{2N+1}^{\text{ass}}(\delta) = -2 \sum_{i=N-\delta+1}^{N+\delta} \frac{1}{i^3}$$

$$-2 \sum_{i=0}^{\delta-1} \left\{ \frac{1}{[(i + \frac{1}{2})^2 + \frac{3}{4} \delta^2]} - \frac{3(i + \frac{1}{2})^2}{[(i + \frac{1}{2})^2 + \frac{3}{4} \delta^2]} \right\}, \quad (15)$$

where the first sum in Eq. (15) stems from intrachain interactions, and the second one from cross chain interactions. The behavior of $\Delta U_{2N+1}^{\text{ass}}(\delta)$ is sketched in Fig. 6. We observe that the energy difference changes sign from negative to positive around $\delta = 2$, which indicates a minimum in energy there, see Fig. 6. This minimum will also persist at large $N$. Indeed, we learn from Eq. (15) that for large $N$ only the interchain correlations will survive. In details, a straightforward summation leads to $\lim_{N \to \infty} \Delta U_{2N+1}^{\text{ass}}(\delta = 2) \simeq -0.0188 < 0$ and $\lim_{N \to \infty} \Delta U_{2N+1}^{\text{ass}}(\delta = 3) \simeq 0.1623 > 0$. Therefore, we can conclude that two symmetrically placed touching chains of length $N + 3$ and $N - 2$ represent an energy minimum for any $N$ larger than two.

3. Summary

Two chains self-assemble in a minimal energy configuration by building short tails of two and a half beads at both ends. This striking and relevant feature is fully consistent with the picture of a single magnet interacting with a chain, see Fig. 1. Thereby, it was indeed shown that the interaction energy becomes negative when the chain has at least six beads ($N_c = 6$ in Fig. 1) corresponding to $N_{\text{tot}} = 2N + 1 = 7$ with $N = 3$), corresponding exactly to two tails of two and a half beads with respect to the touching single magnet. In the next section, we will look for the overall ground state at prescribed
FIG. 7: Reduced energy per particle profiles as a function of the total number of particles \( N_{\text{tot}} \). Ground states are as follows: one chain \((2 \leq N_{\text{tot}} \leq 26)\), two chains \((27 \leq N_{\text{tot}} \leq 128)\), and three chains from \( N_{\text{tot}} \geq 129 \).

FIG. 8: Typical ground state microstructures for different total number of particles \( N_{\text{tot}} \). (a) One-chain configuration for \( N_{\text{tot}} = 25 \). (b-f) Individual chain composition (from top to bottom) are indicated as \((N_1, N_2), (N_1, N_2, N_3)\) (from left to right) for two- and three-chain configurations, respectively. (b) Two-chain configurations for \( N_{\text{tot}} = 100, 101 \), respectively. (d-f) Three-chain configurations for \( N_{\text{tot}} = 150, 151, 152 \), respectively.

IV. GROUND STATE STRUCTURE OF SELF-ASSEMBLY

A. Energy minimization with genetic algorithm

In that numerical part of the work, the reduced potential energy of interaction \( U_{\text{tot}}^{\text{N}} \) has been minimized by evolving transient configurations on a triangular lattice using genetic algorithm. In order to increase the chance of finding the ground state, we typically employ many independent populations of about 1000 initial configurations consisting of individual particles positions. The particle occupation on the triangular lattice is mapped on an array of 0s and 1s, meaning a particle is present at a certain position on lattice or not, respectively. The evolution starts from a population of randomly generated individuals (i.e., configurations), and consists of an iterative process of creation of the new generations. In each generation, the potential energy of interaction \( U_{\text{tot}}^{\text{N}} \) is evaluated for every individual in the population. The prime difference to usual deterministic minimization procedures is that multiple individuals are evolved in each step in a stochastic manner: A number of the best configurations are selected from the current population and modified (recombined and possibly randomly mutated) to form a new generation. The algorithm terminates when a prescribed maximum number of generations has been produced and no more improvement of the best individual(s) is achieved.

B. Numerical results

The overall ground states at prescribed number of constitutive magnets \( N_{\text{tot}} \) were also independently computed using a genetic algorithm. The resulting energy profiles for one chain, two and three touching chains are depicted in Fig. 7. Corresponding illustrative microstructures are sketched in Fig. 8. The energy profile for the single chain structure stems from Eq. 6 whereas that for two touching chains was generated using Eqs. 9 and 13 for even and uneven number of particles respectively. In concordance with the magnetic energy analysis of two-chain states, see Fig. 3 and 5, minimization procedure based on genetic algorithm confirms, for \( N_{\text{tot}} > 26 \) (see Fig. 7), that the ground states correspond indeed to either

(i) two touching equally long parallel chains shifted by two and a half beads for even \( N_{\text{tot}} \), see Fig. 8(b) for illustration,

(ii) or two symmetrically placed chains with \( N + 3 \) and \( N - 2 \) beads for uneven \( N_{\text{tot}} = 2N + 1 \), see Fig. 8(c) for illustration.

For \( N_{\text{tot}} = 26 \), the energy per bead for the one-chain structure is \( u_{26}^{(1-\text{chains})} \approx -2.2791 \) whereas for the two-chain structure \( u_{26}^{(2-\text{chains})} \approx -2.2781 \) is found. For \( N_{\text{tot}} = 27 \), we have \( u_{26}^{(1-\text{chains})} \approx -2.2836 \) against \( u_{26}^{(2-\text{chains})} \approx -2.2889 \).

Finally, we were able to locate the transition at \( N_{\text{tot}} = 129 \) by means of genetic algorithm, cf. Fig. 7. More specifically, at \( N_{\text{tot}} = 128 \), the energy per bead for

number of magnets \( N_{\text{tot}} \), and especially locate the regime of two-chain assemblies.
the two-chain structure is \(u_{12}^{(2\text{-chains})} \approx -2.5182\) whereas for the three-chain structure \(u_{12}^{(3\text{-chains})} \approx -2.5178\) is found. At \(N_{\text{tot}} = 129\), we have \(u_{129}^{(2\text{-chains})} \approx -2.5187\) against \(u_{129}^{(3\text{-chains})} \approx -2.5189\). Representative microstructures are depicted in Fig. 8(d-f), where it can be clearly identified that the (long) mid-chain is always sandwiched by two shorter chains.

V. CONCLUDING REMARKS

We have analyzed the self-assembly of magnetic spheres under strong magnetic field in two dimensions. Chains and assembly of chains constitute the typical microstructures of magnetic beads. A simple but highly instructive situation concerns a single magnet (i.e., a monomer) interacting with a magnetic chain. An effective attraction, even with a dimer, sets in at very short separation as a result of dipole-dipole correlations and excluded volume effects. Nevertheless, a negative magnet-chain interaction energy is solely obtained for a long enough chain.

It turns out that the case of two-chain ground state structures possesses strong symmetry. This feature has allowed us to undertake exact analytical considerations about the behavior of the global potential of interaction. We have demonstrated that the attraction of parallel magnetic chains is essentially a near field effect (i.e., a range of the order of the magnetic monomer) and its strength strongly depends on chain length and relative position. In the far field limit, magnetic chains behave as super dipoles as expected. Besides, we have brought to light tail creation as a mechanism for reduction (more negative) of the cohesive energy. A general result, which holds independently of number of particles, is that minimal energy is achieved if the tails have length of two and a half beads. In the case of even number of particles we obtain a two-fold symmetric ribbon made up of two shifted like-sized chains. For uneven number of particles, we obtain hat-like structures exhibiting a mirror symmetry.

Ground states of self-assembled magnets have been addressed by genetic algorithm. The resulting phase diagram (energy per bead vs the total number of beads \(N_{\text{tot}}\)) has the following characteristics:

- At moderate number of beads \(2 \leq N_{\text{tot}} \leq 26\), it is the one-chain assembly that possesses the lowest energy.
- When \(27 \leq N_{\text{tot}} \leq 128\), it is the two-chain assembly that possesses the lowest energy.
- The two- to three-chain transition occurs at \(N_{\text{tot}} = 129\).

Note that analog findings to the three-chain structure were recently published [19] in three dimensions, where straight long magnetic chains develop a rodlike structure with a narrow rectangular section.

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[20] We have carefully checked that the deepest minimum for \(0 < \delta_x < 1\) occurs at contact and for \(\delta_x = 0.5\) as intuitively expected.
[21] \(\Delta U_{\text{NN}}^{\text{tot}}(\delta)\) can also be seen as the backward discrete derivative of \(U_{\text{NN}}^{\text{tot}}\) with respect to \(\delta\).
[22] Using a genetic algorithm in the next section it will be confirmed that ground state configurations (i.e., with minimal energy) belong indeed to this family of structures.
[23] A similar conclusion could be drawn for like sized chains, see Fig. 8.