Behaviour of magnetic Janus-like colloids

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Abstract
We present a theoretical study of Janus-type magnetic particles at low temperature. To describe the basic features of the Janus-type magnetic colloids, we put forward a simple model of a spherical particle with a dipole moment shifted outwards from the centre and oriented perpendicular to the particle radius. Using direct calculations and molecular dynamics computer simulations, we investigate the ground states of small clusters and the behaviour of bigger systems at low temperature. In both cases the important parameter is the dipolar shift, which leads to different ground states and, as a consequence, to a different microscopic behaviour in the situation when the thermal fluctuations are finite. We show that the head-to-tail orientation of dipoles provides a two-particle energy minima only if the dipoles are not shifted from the particle centres. This is one of the key differences from the system of shifted dipolar particles (sd-particles), in which the dipole was shifted outwards radially, studied earlier (Kantorovich et al 2011 Soft Matter 7 5217–27). For sd-particles the dipole could be shifted out of the centre for almost 40% before the head-to-tail orientation was losing its energetic advantage. This peculiarity manifests itself in the topology of the small clusters in the ground state and in the response of the Janus-like particle systems to an external magnetic field at finite temperatures.

Keywords: magnetic colloids, Janus particles, ground states, self-assembly

(Some figures may appear in colour only in the online journal)

1. Introduction

Smart materials, whose behaviour can be controlled by external fields of moderate and low strengths, form one of the main challenges in soft matter today. Colloids play a significant part in the design of such smart materials and provide a broad range of tuning possibilities, one of which is an applied external magnetic field. In order to design magnetically-controllable colloidal systems, one needs to understand what the internal structure of such materials is depending on the properties of individual colloids. The characteristic sizes of the magnetic colloids can vary from several Ångström to tens of microns, so their internal structure is not always easily accessible experimentally. Besides this, the huge variety of possible compounds and granulometric compositions make the experimental studies highly time consuming. In other words we are facing a clear demand for theoretical predictions (analytical and/or in computer simulations) about the interconnection between a certain microscopic structure of magnetic colloids and their macroscopical behaviour in ensembles.

One of the key properties to be controlled in smart colloidal systems is the self-assembly, as the latter can drastically change the thermodynamic response of the systems. Being able to govern the self-assembly in magnetic colloids allows one to produce tailor-made materials. For magnetic colloids, one traditionally tries to use the simplest approach to study the self-assembly, i.e., to employ the model of dipolar hard spheres (DHS) (diameter \( d \), possessing a point dipole moment \( m \) in their centres) [2–11]. All these works, step-by-step, revealed a hierarchical self-assembly of DHS on cooling: at room temperature they form a gas phase, then, with decreasing temperature \( T \), the particles start forming chains, which at low temperatures collapse in rings or form branched structures, depending on the DHS concentration. The behaviour of DHS has given rise to an idea that by altering the model itself, one can obtain a system showing profoundly different structural transitions and, as a
consequence, qualitatively different macroscopic behaviour. One can modify the DHS model theoretically in two possible ways: firstly, to change the properties of the carrier and to introduce a certain magneto-elastic coupling into the system; for example, this can be done for magnetic gels [12–14], magnetoelastomers [15, 16] or magnetic filaments [17, 18]; secondly, to keep the carrier matrix simple, but to modify the particles themselves [1, 19–25]. The latter modification can come in a number of forms: the shape of the particle can be anisotropic, for example, spheroids, rods and spherocylinders [26, 27], or one can manipulate the positioning of the dipole within the spherical particle, such as with capped colloids [23] or magnetic Janus particles [28].

Janus particles, taking their name from the god Janus with two faces, vastly gain in weight among smart colloids showing not only a particular type of self-assembly, but also a very correlated response to various external drives. In this manuscript we present a simple theoretical model for magnetic Janus particles. Experimentally, in magnetic Janus particles, the two faces are the magnetic and non-magnetic hemispheres. These particles were proposed for the building of 3D hydrogel superstructures with chemically and magnetically tunable complexity for tissue engineering and sensing applications [29]. Alternatively, driving the rotations of such colloids opens new perspectives in biomedical and technological applications [30]. Magnetic Janus particles can be synthesised in various ways: by oil-in-water emulsion [31], microfluidic droplet templating [29, 32] or spin-coating methods [33]. Applying an external electric or magnetic field one can assemble such magnetic Janus particles in staggered chains, chain-like or mesh-like superstructures, and double and staggered chains. While a magnetic field serves to magnetise the caps and manipulate the particles, the influence of an electric field can be of two origins. Firstly, the semiconducting nature of Fe₃O₄ makes it responsive to an AC electric field [34]; secondly, if the non-magnetic part of the particle has an electric dipole, whose orientation is bound to that of the magnetic moment, as in the work [33], the magnetisation of the system can be manipulated by an electric field. Detailed analyses of the structures observed in magnetic Janus particles can be found in the works [34–37]. As for the theory of magnetic Janus particles, to our knowledge there is only one work [25] addressing the subject; however, its focus is shifted away from Janus particles and the investigation sheds light on the self-assembly of sd-particles (particles with dipoles shifted radially outwards out of the particle centre of a mass) with various dipolar orientations.

We would, in contrast, aim at investigating only one possible dipolar orientation and use the shift of the dipole, which in Janus particles corresponds to the size of the magnetic side, as a control parameter to investigate both ground state structures and thermodynamically equilibrium self-assembly. The manuscript is organised as follows. The first section is dedicated to the ground states of small clusters. In the second section we study the structural properties of magnetic Janus-like particles both with and without an applied magnetic field at room temperature. The manuscript ends with a brief summary and outlook.

2. Ground states: small clusters

We investigate a quasi 2D system, in which all particle centres are fixed in one plane, whereas the dipoles are free to rotate. The choice of this geometry was driven by the experimental approaches used for investigations of magnetic colloids, such as cryo-TEM [38] or optical, scanning electron, and atomic force microscopies [34, 35]. In the first step we assume particles (diameter d) to have a permanent dipole moment m shifted out of the particle centre (by the dimensionless value of the shift \(s = 2S/d\)) and oriented perpendicular to the particle radius (which more closely corresponds to the system studied in [31]). For two particles, the geometry is presented in figure 1. Introducing \(x = \sin[(\psi - \phi)/2]\) and \(y = \sin[(\psi + \phi)/2]\) an interparticle magnetic dipole–dipole interaction between two Janus-like particles at close contact can be written in the following form:

\[
U_{dd}^{J}(s, x, y) = \frac{s^2x^4 - 2sx^3y + (s^2 + 1)x^2 - 2sxy + 3y^2 - 2}{(s^2x^2 - 2sxy + 1)^{3/2}}.
\]  

Note that in contrast to the interaction of two particles with central dipoles, the interdipolar distance changes depending on the mutual orientations of the dipoles. The units of this interaction are that of the ratio \(m^2/d^3\). For the Janus-like particles, the head-to-tail configuration is described by \(\phi = \psi = \pi/2\). Minimising the energy (1) we obtain that the energetically advantageous configurations are very different from those of the central dipoles and drastically change with the growing value of the shift \(s\). In figure 2 we plot the ground state energy of the Janus-like particles as a function of this shift, together with sketches of the ground state configurations.
is formed and the energy diverges fast to state only for for the Janus-like particles, the head-to-tail orientation is the ground
Figure 2. The energy of the particle pair as a function of the shift $s$: for the Janus-like particles, the head-to-tail orientation is the ground state only for $s = 0$. For high shifts, the antiparallel pair of dipoles is formed and the energy diverges fast to $-\infty$. The zipper configuration never provides a ground state; rather a perturbed chain configuration to become a ground state (see inset of figure 3), even at very small shifts, the standard head-to-tail orientation is not the most energetically advantageous. Its energy of such a ‘perturbed’ chain (pc) can be written as:

$$U_{pc}(s) = \frac{-1}{4(1 - s^2)^\frac{3}{2}};$$

and a configuration with both dipoles being on one side of the particle centre–centre radius-vector and in an almost head-to-tail configuration. In the latter the distance between the dipoles is smaller than in the zipper, but the orientation is not perfectly energetically advantageous. Its energy of such a ‘perturbed’ chain (pc) can be written as:

$$U_{pc}(s) = \frac{2}{s^2} \left( \frac{2 + \sqrt{1 + 6s^2 - s^4}}{2 - \sqrt{1 + 6s^2}} \right), \quad s \leq 0.4.$$ \hspace{1cm} (3)

As one can see in figure 2, the absolute value of the $U_{pc}$ is always smaller than that of $U_z$. Thus, the zipper does not provide a ground state for two particles. For a larger shift, however, similar to the sd-particles, the Janus-like particles form antiparallel pairs, with the energy:

$$U_{ap}(s) = \frac{-1}{(1 - s)^3}.$$ \hspace{1cm} (4)

Three-particle ground states can be also calculated analytically. For this, we used the approach developed in the work [8]: we first made molecular dynamics simulations to make the list of possible ground state configurations; next, we analytically calculated and compared these energies. The results are presented in figure 3.

The presence of the third particle helps the zipper configuration to become a ground state (see inset of figure 3), albeit for a very small range of the shifts $s$. When the $s$ grows, the triangular alignment of the dipoles provides the ground state configuration. This symmetry only breaks for very high values of shifts, when two particles form an antiparallel pair and the presence of the third one becomes almost irrelevant with its energetically best orientation being the head-to-tail one with respect to one of the two members of the antiparallel pair. The corresponding candidate energies can be written in simple forms:

- the zipper

$$U_{zip}(s) = -\frac{17}{4\sqrt{(1 - 4s^2)^2}};$$ \hspace{1cm} (5)

- the energy of the triangular configuration

$$U_{tri}(s) = \frac{5}{4} \left[ \frac{3}{(1 - \sqrt{3}s)^3} + \frac{\sqrt{3}s}{(1 - \sqrt{3}s)^5} \right];$$ \hspace{1cm} (6)

- one antiparallel pair and a particle forming a zipper with one of the two others—member of the antiparallel pair

$$U_{apz}(s) = -\frac{1}{(1 - 2s)^3} + \frac{4s^2 - 2s - 5/4}{\sqrt{(4s^2 - 2s + 1)^2}} + \frac{5}{4}.$$ \hspace{1cm} (7)
For larger clusters it is not feasible to minimise the energies analytically, which is why we used molecular dynamics simulations more extensively and employed parallel tempering in the work package ESPReSso [39] to elucidate the structures formed at very low temperatures. We studied clusters made from four to seven particles and discovered the structures presented in figure 4. In order to quantitatively follow the transitions we plot the total and magnetic energies of the clusters as obtained from the computer simulations and compare them to that of ideal rings [8]. Once the simulation data starts being lower than the theoretical prediction, the shift at which the structural transition takes place is found. Thus, for four particles, the ring structure continues to be the most energetically advantageous one until very high values of shift. In the case of a five-particle cluster, for shifts higher than 0.4 of the radius, the ring splits into a triangle and an antiparallel pair. Their mutual interaction is very weak. In the same range of the shift values (slightly smaller $s \sim 0.35$) the six-particle ring becomes less energetically advantageous than two triangles. For very high shifts these triangles split into three antiparallel pairs. The interaction between the triangles and pairs in this case is also very low, which leads to basically degenerated ground states (the position of the pairs is irrelevant). The shift at which the seven-particle ring stops being in the ground state is even lower ($s \sim 0.3$). At higher shifts the ring splits into a triangle and a four-particle ring. Their interaction is again weak, so that their mutual orientation basically does not contribute to the energy of the ground state. At even higher shifts the second transition will take place, namely the four-particle ring will split into two antiparallel particle pairs.

Thus, the main conclusion of this section is the following. For two particles, the energetically most advantageous configurations are the perturbed chain, in which a shorter distance between the dipoles provides a larger energy gain than the loss due to the imperfect head-to-tail orientation, if the shifts are small; for larger shifts two particles tend to orient their dipoles antiparallelly. The three-particle ground states are the zipper, the triangle and the antiparallel pair with the third particle, which is almost irrelevant. These findings allow us to predict the structures of small cluster ground states as the two- and three-particle ones play the part of building blocks. In the next section we will consider if there is any reminiscence of the ground state structures in the thermodynamic behaviour of the larger systems of Janus-like particles.
3. Finite temperatures

We start our investigation considering the system of Janus-like particles in the absence of an external magnetic field. We perform molecular dynamics simulations using 512 particles in a full 3D periodic system with metallic boundary conditions in ESPReSso [39]. This is done in order to speed up the calculations of dipolar interactions and using the standard 3D dipolar Ewald summation [40]. However, being interested in quasi-2D systems, we fix all the particle centres in the plane perpendicular to the z-axis of the box. For proper calculations of the dipolar forces we apply dipolar layer correction [41]. To mimic steric repulsion, we use a standard Weeks–Chandler–Andersen potential [42] with the dimensionless $\sigma = d = 1$ and the energy scale $\epsilon = 1$. The shift of the dipole moment is realised by employing virtual sites [1], whose special feature is the following: the forces and torques acting on the virtual sites are calculated in a regular way, but the displacement is not performed. Rather, the latter forces and torques result in the corresponding motion of the particle centre of mass. We study two different particle area fractions by changing the box size: $0.1$ and $0.01$. The dimensionless temperature is fixed to $T^* = 1$. Six different values of the shift are investigated $s = 0.2 \ldots 0.7$ with the $0.1$ step. The value of the dimensionless particle dipole moment is fixed to $(m^*)^2 = \lambda = 5$. This value of $\lambda$, if applied to the soft dipolar spheres with the central dipole, would lead to a relatively strong chain formation, but the transition to ring-like or more complex structures would not yet be pronounced [11, 43]. In figure 5 we present four simulation snapshots. Even for small values of shift ($s = 0.2$) the clusters formed are different from simple chains. That makes this system rather different from that of sd-particles [44], where only chain structures are observed up to shifts $0.4$. With a growing shift, the topology of the aggregates deviates even more from linear chains, so that at $s = 0.4$ (figure 5(b)) some rings and compact structures can be observed. The diversity of the structures drops abruptly when the shift exceeds $0.5$; one can see that basically all the particles are aggregated in three-leaf clovers (figure 5(e)), which are to be replaced by antiparallel pairs once the shift becomes larger (figure 5(d)).

To quantify this transition, we plot radial distribution functions (RDFs) for both centres of the mass (figure 6 (left)) and for the positions of the dipoles (figure 6 (right)).

For small shifts, the RDFs are very similar to those of dipolar soft spheres with chains. However, looking at the position of the first peak of the RDF for the dipolar positions, one finds the distance shorter than the one between the centres of the mass, which corresponds to the zipper-like configurations. When the value of the shift increases, the growing split of the first peak can be observed (both for the centre–centre RDF and the dipolar position one). This corresponds to the appearance of non-linear structures, as the first part of the split peak corresponds to the antiparallel pairs, and the second one to the neighbours in a triangle. The height of the peak grows dramatically with $s$. This is related to the enhancement of the interactions due to the fact that the dipoles can reach a shorter distance between each other. For lower densities, we observe no qualitative change in the structures.

An important conclusion one can draw from this analysis is that the zipper structures can be observed at moderate dipolar strengths (compared to the thermal fluctuations), but only for rather small values of the shift $s$.

For the next step, we apply an external magnetic field along the $x$-axis of the simulation box. The dimensionless value of the magnetic field we denote as $H^*$. In this case, each dipole moment interacts with an applied field and tries to minimise the Zeeman energy $-\langle H^*, m^* \rangle$ by means of coaligning with the $x$-axis. In contrast to the case of the central dipoles, the head-to-tail orientation is not the most energetically advantageous when the dipolar shift $s$ is rather big. So, one can see how the competition between the Zeeman and the dipolar energy leads to a slow structural change. In figure 7 from the top to the bottom the magnetic field strength increases; the shift value grows in each row from the left to the right. The main visual conclusion that follows from figure 7 is that the external field cements the formation of the zippers, but the the interparticle distance within the zipper strongly depends on the value of $s$. To scrutinise the latter dependence, we plot the radial distribution functions in figure 8.

The field tries to break the structures with a closed dipole moment. The closer the dipoles are to the particle surface, the larger the value of $H^*$ is needed to realign the particles, as the effective energy of the compact structures grows with an increasing $s$. Indeependently from the shift value, though, for high fields the linear zipper structures are formed, in which the dipoles are coaligned with the field and oriented head to tail. This can be seen when examining the left column of figure 8, where from the top to the bottom the curves become more and more similar regardless of the value of the shift. The fact that the cluster formation takes place at high fields makes the systems of Janus-like particles in a way similar to that of ordinary dipolar soft spheres, where the field leads to enhanced chain formation. On the other hand, the formation of linear structures at high fields underlines again the difference between the Janus-like colloids studied here and the sd-particles (capped colloids), in which the dipole is shifted outwards radially: in the latter with the growing field intensity the cluster formation becomes more-and-more suppressed.

Looking at the right-hand column in figure 8 and analysing the RDFs for the dipolar positions, one can notice that for the highest $s$ the shape of the first peak changes with the field, reducing the split. This corresponds to the breaking triangles and antiparallel pairs occurring when the the Zeeman energy becomes larger than that of the magnetic dipole–dipole interaction. Note also that the position of the peak shifts to the left with a growing shift. The latter allows us to estimate the dependence between the next-nearest neighbours in the zipper and compare it to the analytical expression obtained from the ground state calculations. The corresponding characteristic zipper angle is plotted in figure 9.

The angle vastly decreases with a growing shift. This dependence on the ground state particle arrangement has the form:

$$\beta = 2 \arccos(s).$$

The angle estimated from the maximum RDF is not exactly the same for several reasons. Firstly, the maximum RDF
Figure 5. Simulation snapshots of the systems of Janus-like particles without an external field. The values of the dipolar shifts $s$ are provided in the plots. The particle area fraction is $0.1$, $\lambda = m^2 / (d^3 k_B T) = (m^*)^2 = 5$ (with $m$ being a real magnetic moment, $m^*$ denoting a dimensionless magnetic moment used in simulations, $k_B$ being a Boltzmann constant and $T$ standing for the real temperature). With a growing $s$ one clearly sees that the cluster topology, as well as the cluster size, change in close correlation with the ground states. The orientation of the dipoles is not shown for the sake of clarity; the positions of the dipole moments are marked as red spheres. (a) $s = 0.2$. (b) $s = 0.4$. (c) $s = 0.6$. (d) $s = 0.7$.

is a collective property and also reflects the presence of other topological structures in the system; secondly, the GS configuration is calculated for hard spheres, whereas in the simulations we use a Weeks–Chandler–Andersen potential to mimic the steric interactions. However, the qualitative shift dependence of the zipper arrangement is preserved.

4. Conclusion

In the present manuscript, we study the behaviour of Janus-like magnetic particles, employing analytic calculations and molecular dynamics simulations. At the first step, we analysed the ground states of small clusters and observed that for small shifts a perturbed chain (for two particles) or a zipper (for three particles) provides the ground state configurations. The range of shifts for these structures, though, is very narrow. If the shift goes above $s > 0.4$, the antiparallel pair for two particles or a triangular arrangement of three particles are the ground states. These configurations remain ground states up to very high shifts. For three particles, when the shift exceeds $0.9$ the degeneration occurs caused by the formation of an antiparallel dipolar pair, making the orientation of the third particle basically irrelevant. The ground states of larger clusters (we studied those formed by four to seven particles) use the two- and three-particle ground states as building blocks. For the lowest shifts, the rings are the ground states, similar to the systems of ordinary dipolar soft or hard spheres. For the highest shifts, the ground state structures are composed of antiparallel pairs. Note that for Janus-like particles there is a small range of shifts $(0 < s < 0.4)$ where the configurations have a non-zero total dipole moment (see the zipper configuration of three particles). The rest of the ground states have a zero total dipole moment, which means that these structures are weakly susceptible to an applied magnetic field. The structural properties at room temperature of Janus-like colloids is studied by molecular dynamics simulations both
Figure 6. Radial distribution functions for the Janus-like particles in the absence of an applied external magnetic field. (left) The centre of
the mass-centre of the mass RDF. (right) The dipole position-dipole position RDF. The particle area fraction is 0.1, $\lambda = 5$. With a growing $s$
onlyline{one clearly sees that the cluster topology as well as the cluster size change and the average cluster size decreases. A log scale is applied
along the ordinate axis.}

Figure 7. Simulation snapshots of the systems of Janus-like particles under the influence of an external magnetic field applied horizontally.
The values of the dipolar shifts $s$ are provided in the plots. The particle area fraction is 0.1, $\lambda = 5$. With growing $s$ and increasing field, the
zipper becomes a dominant structure leaving out the other ground state ones. (a) $s = 0.2$, $H^* = 0.5$. (b) $s = 0.4$, $H^* = 0.5$. (c)
$s = 0.7$, $H^* = 0.5$. (d) $s = 0.2$, $H^* = 2.5$. (e) $s = 0.4$, $H^* = 2.5$. (f) $s = 0.7$, $H^* = 2.5$. (g) $s = 0.2$, $H^* = 4.5$. (h)
$s = 0.4$, $H^* = 4.5$. (i) $s = 0.7$, $H^* = 4.5$. (j) $s = 0.7$, $H^* = 4.5$. 

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Figure 8. Radial distribution functions for the Janus-like particles in an applied external magnetic field (value $H^*$ is provided in each plot). (left) The centre of the mass-centre of the mass RDF. (right) The dipole position-dipole position RDF. The particle area fraction is 0.1, $\lambda = 5$. For high fields the zipper structure dominates independently from the value of $s$. However, the distance between the particles in the zipper strongly depends on the dipolar shift.

with and without an applied magnetic field. We show that the dipolar shift exerts a crucial influence on the self-assembly: both the cluster size and the cluster topology change. Thus, in the absence of an externally applied magnetic field, for a small shift, zipper-like structures are observed with predominantly head-to-tail orientation of dipoles. For large shifts the clusters become compact: pairs or three-leaf clovers. The external magnetic field tries to break compact structures and cements the zippers. The characteristics of the zipper depend both on the shift and on the field strength.
Figure 9. The dependence of the characteristic zipper angle on the dipolar shift. The simulation results are presented in symbols; the ground-state configuration angle is plotted as a solid line. In the simulations, the particles can be at shorter distances due to the softness of the Weeks–Chandler–Andersen potential.

We are currently working on the density functional approach to quantify the cluster analysis and scrutinise the microstructural peculiarities of Janus-like systems. It is worth mentioning that the behaviour of the model colloids presented here corresponds to that of real magnetic Janus particles, which is why this simple model can be applied to predict their properties [34–37]. Namely, model Janus particles exhibit a transition from a more closed zipper to that with a larger centre–centre distance depending on the shift (an analogous transition was observed in [35], where the change in the zipper was caused by varying the disposition rate, or by applying an ac electric field [34]). As for the field-free case, the structure of the clusters is rather similar to that obtained in the work [31], where the particles had a permanent magnetic moment. However, we are planning to introduce the polarisability of the particles in theory, rather than using a permanent dipole moment in the future.

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