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PAPER

Ferrofluids with shifted dipoles: ground state structures

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In the past decades, ferrofluids have become relevant in many applications ranging from engineering to medicine, and have attracted the interest of scientists from many fields. To understand the physical mechanisms serving as a basis for these applications, over the last decades, many of the properties of ferrofluids have been studied and can now be controlled. However, in order to fine-tune various aspects of the interactions in the system and hopefully – in the long run – to build tailored structures, in recent years, magnetic nanoparticles and colloids that deviate from the model of a spherical particle with a dipole moment at its center were examined. Among them are dumbbells, magnetic core-shell particles, elongated ferro-particles, and colloidal particles with a magnetic cap. In this paper, we introduce and examine – using analytical calculations and Monte Carlo simulations – one such model system, namely, magnetic particles in which the dipole moment is shifted from the center of mass towards the particle's surface. In this way, an additional anisotropy is introduced to the particles, which results in quite different and surprising microscopic properties of suspensions. Here, we mainly concentrate on ground states of small clusters of shifted-dipole particles, but also take a first glance on suspensions at finite temperature.

1 Introduction

Ferrofluids are suspensions of magnetic particles in a magneto-passive carrier liquid. The suspended particles usually have a size of the order of 10 nm, so they consist of a single magnetic domain. In other words, each ferroparticle has a permanent magnetic moment (**m**), the orientation of which within a particle is determined by the structure of the material, and the value of this moment (*m*) is proportional to the particle volume. To keep ferroparticles from irreversible aggregation and sedimentation, they are stabilized either by a layer of surfactant in case of oil based carriers or by electrostatic stabilization in aqueous suspensions. The typical volume fractions achievable during the synthesis are below 10%. Particles in the fluid are free to rotate and are involved in active Brownian motion, thus, magnetic fluids exhibit superparamagnetic behaviour: they have zero magnetization in the absence of an external field, and can be noticeably magnetized by the external magnetic field due to the alignment of particle magnetic moments along the field direction. This alignment can be reached in two ways: either by a rotation of the entire particle – called Brownian relaxation – or by a rotation of the magnetic moment within the particle – the so-called Néel relaxation, where the probability for the latter decreases exponentially with increasing volume of the particles'

magnetic core. In the past decades, ferrofluids and magnetic colloids have become relevant in many applications ranging from engineering to medicine, and have attracted the interest of scientists from many fields. Ferrofluids are employed, *e.g.*, as seals around rotating shafts,¹ for delivering drugs to tumors,² monitoring the dynamics of antibody reactions,³ and for tomography.⁴ Many of these applications rely on the ability to control the properties and dynamics of the fluid by an external magnetic field, or to probe them using sensors, making it important to understand the microstructure of ferrofluids itself, and how it influences macroscopic properties. Examples of the experimental tools available for this purpose are numerous, but provide only implicit knowledge about the microstructure: small angle neutron scattering,^{5–8} magnetic birefringence measurements,^{9–12} magnetoviscous effect^{13–15} (change of a ferrofluid's viscosity when an external magnetic field is applied) investigations, diffusion coefficient analysis.¹⁶ “*In vivo*” observations of ferroparticle clusters is only possible in thin films where Cryo-TEM can be used.¹⁷

The theoretical description of the thermodynamic-equilibrium microstructure of ferrofluids is traditionally based on the density functional approach,^{18–23} integral equations,^{24,25} or direct calculations^{26–29} of pair correlation functions for various model systems such as mono- or polydisperse spherical ferroparticles in different geometries. Recently some theoretical analysis of ferrofluid ground states in thin layers also became available.³⁰

Being a complex problem, ferrofluid microstructure investigations turn out to be perfectly suitable to be handled by computer simulation techniques. Usually in computer

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simulations magnetic nanoparticles are modeled as hard or soft spheres which additionally interact *via* a dipole–dipole potential, in other words, a so-called coarse-grained approach is employed. In this way systems with different geometries, densities and interaction strengths were investigated by many authors for more than 15 years, here we provide only few of these works and address references there in.^{31–39}

As many of the properties of these systems are now understood, in recent years, magnetic nanoparticles and colloids that deviate in one way or another from the spherical shape were examined. Some examples are dumbbells, *i.e.*, two overlapping spheres of opposite charges,⁴⁰ magnetic core-shell particles,⁴¹ elongated ferroparticles,⁴² and colloidal particles with a magnetic cap.⁴³ All these models allow fine-tuning of various aspects of the interactions in the system with the hope of understanding the peculiarities of magnetic nanoparticles clustering, and – in the long run – building tailored structures.

In this contribution, we introduce and examine another “unusual” model system, namely, magnetic particles in which the dipole moment is shifted from the centre of mass towards the particle’s surface. In this way, an additional anisotropy is introduced to the particles, which results in quite different microscopic properties of suspensions. We call such particles – “sd-particle”, to abbreviate the term shifted dipole particles. Although sd-particles are an abstract model, they show similar structures to those found for colloids with a magnetic cap⁴³ and they help us to further understand peculiarities of the dipole–dipole interaction.

In the following sections, first, the model is presented (section 2) and the interaction between two and three sd-particles is discussed in detail using analytical calculations and simulations, allowing us to get an understanding of how neighboring particles influence each other (section 3, 4). In section 5, we explain the Monte Carlo simulation technique we use, and present results for the ground state of small clusters. We conclude our contribution with a first glance at magnetization properties of suspensions at finite temperatures in section 6.

2 Model

In simulations and analytical calculations, magnetic nanoparticles are typically modeled as hard or soft spheres with a magnetic dipole moment located at their centre. They interact *via* the dipole–dipole interaction

$$U_d(ij) = -\frac{\mu_0}{4\pi} \left[3 \frac{(\mathbf{m}_i \cdot \mathbf{r}_{ij})(\mathbf{m}_j \cdot \mathbf{r}_{ij})}{r^5} - \frac{(\mathbf{m}_i \cdot \mathbf{m}_j)}{r^3} \right],$$

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j, |\mathbf{r}_{ij}| = r,$$

where μ_0 is the vacuum permeability and $\mathbf{m}_i$ and $\mathbf{m}_j$ are the dipole moments of the particles, respectively. This interaction for the case of hard spheres (the minimal distance between two dipoles in this case is determined by the hard sphere diameter) has its global minimum, when the particles are touching and the dipole moments together with the displacement vector $\mathbf{r}_{ij}$ are aligned parallel. A second – local – minimum is found, when the dipole moments are aligned anti-parallel and the vector connecting the center of the particles is perpendicular to the dipole moments. This local minimum will become important for sd-particles.

In sd-particles – the model we introduce in this contribution – the dipole moment is not located at the centre of mass of the particle but it is rather shifted outwards towards the particle’s surface, while still pointing outwards, parallel to the vector connecting the centre of mass and the position of the dipole moment. Thus, the particle is symmetric with respect to a rotation around the vector pointing from centre of mass to the dipole moment. The most important consequence of the shift of the dipole moment is that the distance between the dipoles now depends on the sd-particles’ orientation.

A sketch of two sd-particles can be seen in Fig. 1. In the next section, we examine the interaction of two and three such particles and find new surprising ground state structures.

3 Interaction of two sd-particles

Even though we do not constrain the magnetic moments in one plane in this paper, in the sections where we theoretically investigate the ground state structures of 2 and 3 sd-particles, we neglect the out of plane fluctuation of dipoles. This approximation is based on the previous studies of ferroparticle ground state structures in quasi-2D systems,³⁰ where it was found that for low temperatures the fluctuations of the moments in the direction perpendicular to the plane in which particle centres were located, vanished. Thus, the model depicted in Fig. 1 can be used to find the ground state structures of sd-particles. The dimensionless interaction energy for the pair of sd-particles can be written as

$$U_{dd}(\varphi, \psi, \alpha) = \frac{\alpha^2 \cos^2(\psi - \varphi)}{(2\alpha^2(1 - \cos(\psi - \varphi)) + 4 + 4\alpha(\cos\varphi - \cos\psi))^{5/2}} - \frac{2\cos(\psi - \varphi)[2\alpha^2 - \alpha(\cos\psi - \cos\varphi) - 2]}{(2\alpha^2(1 - \cos(\psi - \varphi)) + 4 + 4\alpha(\cos\varphi - \cos\psi))^{5/2}} - \frac{6[\alpha(\cos\psi - \cos\varphi) + 2\cos\varphi\cos\psi] + 3\alpha^2}{(2\alpha^2(1 - \cos(\psi - \varphi)) + 4 + 4\alpha(\cos\varphi - \cos\psi))^{5/2}} \quad (1)$$

Fig. 1 This figure illustrates the geometry that we consider for two interacting sd-particles of radius R . Both dipole moments are placed at a distance d from the respective particle’s centre. Both particles can rotate, and the dipole vector always points outwards radially. The distance between the dipole moments is denoted by r_{12} . φ is the angle between the z axis and the second magnetic moment, m_2 , and ψ is the angle between the z axis and the first magnetic moment, m_1 .

Here, α is the shift of the dipole moment d divided by the particles' radius R , ψ and φ are the angles between the z -axis and the orientation of the first and second particles' magnetic moments, respectively. This energy, as well as every energy below, is normalized by the value $\mu_0 m^2 / (4\pi R^3)$.

By minimizing eqn (1) with respect to the angles ψ , and φ , we find the ground state configuration as a function of the dipole moments' shift α . For no shift ($\alpha = 0$), the global minimum and maximum correspond to the head-to-tail orientation and head-to-head configuration of moments, respectively. This minimum

$$\psi(\alpha) = 0, \varphi(\alpha) = 2\pi,$$

albeit continuously flattening with increasing shift, remains the global one up to the value $\alpha = 0.408$. This can be seen in the first part of Fig. 2a, where the angles φ and ψ in the ground state are plotted as a function of the relative shift α . After the shift reaches $\alpha = 0.408$ the configuration of dipoles changes drastically. This is because the energy of the previous local minimum has decreased and became equal to the energy of the global minimum. Thus, one can see in Fig. 2a, that, without loss of generality, the moment of the upper particle in its ground state configuration starts rotating clockwise with increasing α . Hence, φ decreases fast from 2π until it reaches the value $\varphi(0.597) \approx 1.2\pi$. By that time the moment of the lower particle moves only slightly and reaches the value $\psi(0.597) \approx 0.2\pi$. Hence, at $\alpha = 0.597$ the moments reach an antiparallel orientation ($\varphi - \psi = \pi$). The description of this second regime can be found only in an implicit form, being too long to be provided here. From $\alpha = 0.597$ on, up to the maximum shift $\alpha = 1$, both moments start rotating symmetrically: the upper one rotates clockwise, and the lower one rotates counterclockwise. This rotation, shown in the last part of Fig. 2a, has the following functional form:

$$\varphi(\alpha) = \pi + \arccos \frac{\alpha^2 - 1 + \sqrt{-\alpha^4 + \alpha^2 + 1}}{\alpha},$$

$$\psi(\alpha) = \varphi(\alpha) - \pi, \alpha = 0.597.$$

The dimensionless interaction energy in the ground state as a function of the shift in the last regime is:

$$U(\alpha) = -2 \frac{(3 - \alpha^2)q(\alpha) + \alpha^4 - 3}{\alpha^2(\alpha^2 - 3 + 2q(\alpha))^2 \sqrt{\alpha^2 - 3 - 2q(\alpha)}}, \quad (2)$$

$$q(\alpha) = \sqrt{-\alpha^4 + \alpha^2 + 1}, \alpha \in [0.597, 1]$$

which goes to $-\infty$ when α approaches 1. This divergence is proportional to $(1 - \alpha)^{-3}$.

This change in ground state configuration is driven by the decrease of the distance between two dipole moments r , which appears in the expression for the energy (eqn (2)) in the power r^{-3} . In consequence, the energy of the ground state at higher shifts α is much lower than that of the original head-to-tail configuration found at $\alpha = 0$. At very high shifts, the dipole moments have an anti-parallel orientation and the vector connecting their positions tends to be perpendicular to the moments' orientation. Thus, the local minimum for $\alpha = 0$, mentioned in the previous section, becomes the global minimum for two sd-particles in the limit of shift $\alpha \rightarrow 1$. The strong decrease in energy of the optimal configuration with increasing shift is plotted in Fig. 2b. The solid curve represents exact analytical calculations, while the dots represent simulation results (see below). The energy of the head-to-tail configuration – which is independent of the shift α – is shown as a dashed line and set to -1 . The total energy is normalized by the value $\mu_0 m^2 / (4\pi R^3)$, where for magnetite particle (with $R \sim 10$ nm) the magnetic moment has an order of 10^{-19} A m². As will be seen in the following sections, this change

Fig. 2 a) Dependence of the particles' orientations φ (solid line) and ψ (dashed line) on the shift in the ground state. There are three different regions: for a shift below 0.408, the angles are constant ($\varphi = 2\pi$; $\psi = 0$). This represents the head-to-tail orientation of the magnetic moments as it is also found in the non-shifted system. For a shift in the interval from 0.408 to 0.597, the angles change differently until the anti-parallel configuration is reached. At this position magnetic moments are symmetric with respect to the line connecting the particle centers. For even larger shifts, the moments keep rotating symmetrically, keeping a constant difference of π (φ reaches π from above, whereas ψ approaches zero from below). With the shift approaching unity, we observe an anti-parallel orientation of the magnetic moments, totally unfavorable for zero shift. To illustrate the configurations we provide particle sketches in the legend. b) Ground state energy for two sd-particles versus the shift. This energy is normalized by the value $\mu_0 m^2 / (4\pi R^3)$. For a typical magnetite particle of 10 nm in diameter its magnetic moment has the order of 10^{-19} A m². We rescaled the plot so that for nonshifted particles the pair head-to-tail configuration energy is equal to -1 . At higher shifts, the magnetic moments of the particles become more anti-parallel aligned, and they approach each other. Since the distance between the dipoles enters with a power of three, this leads to a strong decrease in ground state energy with increasing shift.

in the energy landscape will result in structure of larger clusters being qualitatively different from what is found in the non-shifted system.

4 Interaction of three sd-particles

To obtain the ground state configurations and energies for three sd-particles, we follow the strategy used in ref. 30. Namely, computer simulations – explained in detail in the next section – were used to obtain approximate ground state structures, which allow to restrict the set of candidates for the ground state. Subsequently, the exact results for the energies of these candidates were obtained analytically. This approach has the advantage of making things simple enough for analytical calculations while avoiding the imprecision of simulation results. In the simulations four regimes were observed: chain, ring, symmetrical up-down-up and asymmetrical up-down-up.

For a chain of n particles, the dimensionless (normalized by the value $\mu_0 m^2 / (4\pi R^3)$) ground state energy can be found in ref. 30:

$$U^{\text{CH}}(n) = -\frac{1}{4} \sum_{k=1}^{n-1} (n-k) \frac{1}{k^3}. \quad (3)$$

For $n = 3$, the energy is $U^{\text{CH}}(3) = -0.531$ and the prefactor by which the energy is normalized is of the order of 10^{-16} J in the case of magnetite particles with a 10 nm diameter. This expression is also valid for the three sd-particle chain up to the shift value $\alpha = 0.258$ (see, configuration 1, Fig. 3), after which the ground state structure is provided by a triangular configuration of particles. For the first and second particle, the angles between the moments and z -axis will be still denoted as ψ and φ , while for the third particle for the corresponding angle we introduce the

Fig. 3 Lowest energy states of small clusters obtained analytically. (Panel 1) At low shifts ($\alpha \in (0, 0.258)$), a chain is formed. At higher shifts (Panel 2) ($\alpha \in (0.258, 0.799)$), one observes a triangular structure of sd-particle magnetic moments, and when the shift increases even further ($\alpha \in (0.799, 0.84)$) (Panel 3), the structure remains symmetrical but the dipole moments assume an up-down-up configuration. For ($\alpha \in (0.84, 1)$) the symmetry breaks and one anti-parallel pair is formed (Panel 4).

notation ξ . It is worth underlining that for three particles the first transition to a structure, different from the one found in the non-shifted system, appears at a lower shift than for two particles.

In the ring or “triangular” configuration (configuration 2, Fig. 3), found from $\alpha = 0.258$ to $\alpha = 0.799$, the energy is a sum of three equal contributions for each pair of particles. *A priori*, we do not know what angle the dipole moments take with respect to the vector connecting the particles’ centres. However, by computer simulations, this angle was found to be the same for all three particles. Hence, we write the energy as a function of this angle, η , and then locate the minimum. The relative distance between two consecutive dipole moments in the ring configuration is:

$$r_{12}^{\text{TR}}(\eta, \alpha) = \sqrt{3\alpha^2 + 4 + 2\alpha(3\cos\eta + \sqrt{3}\sin\eta)}. \quad (4)$$

Inserting this expression into eqn (2), the dimensionless energy can be written as

$$U^{\text{TR}}(\eta, \alpha) = \frac{3}{r_{12}^{\text{TR}}(\eta, \alpha)^5} \left[\frac{21}{4}\alpha^2 + (3\cos\eta + \sqrt{3}\sin\eta)\frac{7}{2}\alpha + 3\sqrt{3}\sin 2\eta + 6\cos^2\eta - 2 \right]. \quad (5)$$

By setting $\partial U^{\text{TR}}(\eta, \alpha) / \partial \eta = 0$, we can find the angle η which provides the minimum of the dimensionless energy for each value of the shift α . The equation for η turns out to be a 3rd order polynomial with respect to α . Thus, Cardano formulas can be used to obtain the implicit dependence of the shift α on η . The inverted dependence normalized by π is presented in Fig. 4 by a solid line. One can see that the function $\eta(\alpha)/\pi$ is linear, and can be approximated by the linear fit $\eta_{\text{app}}(\alpha)/\pi = 0.427\alpha + 0.67$, which is plotted in fig. 4 as a dashed line.

Thus, the magnetic moments of the particles keep rotating “inward” forming a triangle, approaching the vectors connecting the particles’ centres (see configuration 2 in Fig. 3, and Fig. 5, where the extremum angles ψ , φ , and ξ are plotted as functions of shift α). Once the shift reaches the value $\alpha = 0.799$ and the angle becomes $\varphi = 1.01\pi$, meaning that the moment has passed already

Fig. 4 The dependence of the extremal angle η/π on the relative shift α . This dependence results from the minimization of the energy for the “triangular” configuration. This configuration provides the ground state for $\alpha \in (0.258, 0.799)$. The solid line represents the exact result, the linear fit $\eta_{\text{app}}(\alpha)/\pi = 0.427\alpha + 0.67$ is plotted as a dashed line.

Fig. 5 The analytical dependence of the angles ϕ/π (red, middle dashed curve), ψ/π (black, upper solid curve) and ξ/π (blue, lower dash-dotted curve) on the value of α . There are 4 qualitatively different regimes, see Fig. 3: a chain with constant energy provides the ground state for $\alpha \in (0, 0.258)$; the next ground state is given by the triangular configuration for $\alpha \in (0.258, 0.799)$; the third interval of shifts is $\alpha \in (0.799, 0.848)$, where the magnetic moment of the 3rd sd-particle is immobile ($\xi/\pi = 1/2$), and the 1st and the 2nd moments rotate symmetrically inwards towards $\psi/\pi \rightarrow 5/3$ and $\phi/\pi \rightarrow 2/3$; the ground state becomes totally asymmetrical at $\alpha = 0.848$ when the moment of the 3rd particle starts rotating towards the moment of the 1st particle $\xi/\pi \rightarrow 2/3$, the moment of the 1st particle keeps rotating counter clockwise $\psi/\pi \rightarrow 5/3$ until the symmetry is partially restored at the value of $\alpha = 0.963$, when $\psi/\pi - \xi/\pi = 1$ and the angles keep changing linearly ($\xi/\pi = 0.644\alpha + 0.023$, $\psi/\pi = \xi/\pi + 1$) decreasing the distance between the moments to zero and driving to an energy divergence similar to the one observed for 2 sd-particles (see, Fig. 2b). In the last regime the moment of the second sd-particle slowly rotates clockwise until $\phi/\pi = 1.264$, after that the rotation stops.

the value of π , when it is antiparallel to $\mathbf{r}_{12}$, an abrupt transition occurs, thus, forming a new symmetrical up-down-up configuration (see, configuration 3, Fig. 3). For this shift the other two angles are $\psi = \phi + 2\pi/3$, and $\xi = \phi - 2\pi/3$. That means that ϕ is slightly bigger than the angle between the z -axis and $\mathbf{r}_{13}$ ($5\pi/3$), and ξ is slightly bigger than the angle between the z -axis and $\mathbf{r}_{32}$ ($\pi/3$).

For the symmetrical up-down-up configuration (SUD), found for $\alpha > 0.799$, without loss of generality, the magnetic moment of the 3rd sd-particle points so that $\xi = \pi/2$, and the moments of the 1st and the 2nd sd-particles rotate inwards, having the same angle between themselves and the line connecting the centers of the 1st and the 2nd particle. Let the angle between the 1st and 2nd particle line of centres and the moment of the 1st particle be $\pi + \gamma$, and the angle between the same line and the moment of the

2nd particle be $2\pi - \gamma$. The energy in this case can be split into three contributions: the interaction energy $U_1^{\text{SUD}}(\gamma, \alpha)$ of the two “outer” dipole moments (namely, the moments of particles 1 and 2), and the interaction energy U_2^{SUD} of each of these outer ones and the central one. The two terms for 1–2 and 1–3 sd-particles’ interaction energy are identical due to the mirror symmetry with respect to the middle axis of the configuration. The expressions for these energies and corresponding distances are:

To find the critical angle γ , we use a procedure similar to the one described above, namely, we solve the equation $\partial U^{\text{SUD}}/\partial \gamma$. We find that the outer particles rotate inwards with increasing shift, while the dipole moment of the third sd-particle remains constant. This is again driven by the fact that the distance between the dipole moments decreases with increasing shift. This symmetrical regime provides the ground state until the critical angle γ reaches the value $\gamma = 0.624\pi$ at $\alpha = 0.848$, thus forming the following configuration: $\phi = 1.376\pi$, $\psi = 1.624\pi$ and $\xi = \pi/2$. When the shift increases further, the symmetry of the system breaks, as shown in Fig. 3 (see, configuration 4). In Fig. 6 the dot products between the dipole moments of three sd-particles for shifts α around the transition to the non-symmetrical regime are

Fig. 6 Dot products between the dipole moments of three sd-particles for shifts α around the transition to the non-symmetrical regime, *i.e.*, the top curve corresponds to the product of moments of particle 1 and 2, and the lowest one to the product of 1 and 3. Up to a shift of ~ 0.848 , the dipole moments of the particles 1 and 2 rotate inwards symmetrically and form the same angle with the moment of the 3rd particle, respectively. For higher shifts, without loss of generality, the magnetic moment of the 3rd sd-particle rotates towards the one of the 1st sd-particles and, thus breaks the mirror symmetry of the configuration. Arrows and numbers on the right side of the picture correspond to the analytically found values of dot products at the limit of the shift value $\alpha = 1$.

$$\begin{aligned}
 U_1^{\text{SUD}}(\gamma, \alpha) &= \frac{2(1 + \cos^2 \gamma)}{r_{12}^{\text{SUD}}(\gamma, \alpha)^3}; \\
 r_{12}^{\text{SUD}}(\gamma, \alpha) &= 2(1 + \alpha \cos \gamma), \\
 U_2^{\text{SUD}}(\gamma, \alpha) &= \frac{-8\alpha(\sqrt{3} - \alpha) + \alpha \sin 2\gamma}{2r_{13}^{\text{SUD}}(\gamma, \alpha)^5} + \frac{\cos \gamma(\sqrt{3} - \alpha)(\alpha \cos \gamma - 3)}{2r_{13}^{\text{SUD}}(\gamma, \alpha)^5} + \frac{\sin \gamma[5 - 4\alpha(\sqrt{3} - \alpha)]}{2r_{13}^{\text{SUD}}(\gamma, \alpha)^5}; \\
 r_{13}^{\text{SUD}}(\gamma, \alpha) &= \sqrt{4 + 2\alpha[(\sin \gamma + 1)(\alpha - \sqrt{3}) + \cos \gamma]}, \\
 U^{\text{SUD}}(\gamma, \alpha) &= U_1^{\text{SUD}}(\gamma, \alpha) + 2U_2^{\text{SUD}}(\gamma, \alpha).
 \end{aligned}
 \tag{6}$$

plotted. We used computer simulations to obtain these dot products and discovered that starting from a certain value of the shift the angle between two shifted dipole moments approaches π , so that the scalar product quickly reaches -1 . Analytically, this last configuration depends on all 3 angles ψ , φ and ξ , and no reduction in degrees of freedom is possible. Therefore, only numerical energy minimization is possible. However, one can still characterize the state quite accurately. The critical value of shift was found to be $\alpha = 0.963$ at which $\psi - \xi = \pi$. For the values of shifts $\alpha \in (0.848, 0.963)$ the angle ψ first drops slightly, reaching the minimal value of $\psi = 1.605\pi$ at $\alpha = 0.866$, and then starts growing again. While the angle ξ grows monotonously, the angle φ decreases monotonously. When the value of the shift reaches $\alpha = 0.963$ the moments of the first and the third particle become antiparallel, and the values of the corresponding angles start growing linearly, keeping their antiparallel alignment: $\xi/\pi = 0.644\alpha + 0.023$, $\psi/\pi = \xi/\pi + 1$, approaching the values $\xi/\pi = 2/3$ and $\psi/\pi = 5/3$, respectively. The angle φ reaches a plateau at the value $\varphi/\pi \sim 1.264$.

To summarise the results of this section, the ground state energy of three sd-particles is plotted in Fig. 7 as a function of the shift value α . In Fig. 5 one can see the dependence of the critical angles on the shift for all 4 regimes. Here, with growing shift, one can see first the transition from the shift-independent chain energy to the energy of a triangular configuration ($\alpha = 0.258$). After the shift α reaches the value 0.799 another sharp transition occurs and the SUD configuration becomes the ground state. The last transition accompanied by the symmetry break takes place at the shift $\alpha = 0.848$. At this value, without loss of generality, the moments of the first and the third particle tend to create an antiparallel pair, which drives to a divergence similar to the one observed for 2 sd-particles in the last regime. After the shift reaches $\alpha = 0.963$ the scalar product of the 1st and the 3rd sd-particle magnetic moments becomes -1 , resulting in the formation of an antiparallel pair. The last step is characterized by the decrease of the distance between the latter two moments ($\psi \rightarrow 5\pi/3$; $\psi \rightarrow 2\pi/3$), while the magnetic moment of the second sd-particle remains almost immobile ($\varphi/\pi = \text{const} = 1.264$).

Fig. 7 The ground state energy of three sd-particles as a function of the shift α (normalized by the value $\mu_0 m^2 / (4\pi R^3)$). The solid line corresponds to the analytical result, simulation data is plotted in rhombs.

So, the ground state of two and three sd-particles strongly depends on the shift. When the value of α is large enough the formation of antiparallel pairs provides the dominant contribution to the energy decrease. Thus, one can expect that a similar behaviour will be observed for any finite number of particles in the system. We provide more detailed analysis of this question in the next section.

5 Ground states of small clusters

In this section, we study small clusters of sd-particles with a size of four to six particles. These are building blocks that help us to understand larger systems. For more than three sd-particles, analytical calculations in most cases become too cumbersome to obtain exact solutions for the ground state structure. Therefore, we examine the structure of small clusters using simulated annealing. We consider clusters in a quasi two dimensional geometry (q2d), *i.e.*, the centres of particles are fixed in the XY plane, while the particles are allowed to rotate freely. For sd-particles, this in principle means that the dipole moment can be located outside the XY plane. We find, however, that for all ground states, analogously to the non-shifted case, the dipole moments lie in the plane of the particles' centre of mass.

Simulated annealing is a heuristic Monte Carlo⁴⁴ scheme to find lowest energy states of a system. It works by continually decreasing the temperature of the system so that it is driven to a minimum in the energy landscape. It is based on a Monte Carlo simulation using the Metropolis algorithm,⁴⁵ in which the configurations of the system are randomly sampled, weighted by their probability in the canonical ensemble, *i.e.* the Boltzmann factor $e^{-U/k_B T}$ – here, U is the energy of the configuration, k_B is the Boltzmann constant and T is the temperature. For each simulation step, the configuration is slightly altered, *e.g.*, by rotating and moving a particle. If the energy difference due to this alteration is less than zero, the alteration is accepted. If the energy is increased, the alteration only is accepted with a probability of $e^{-\delta U/k_B T}$, where δU is the energy difference. The precise manner of altering the system is not important, as long as detailed balance is fulfilled. It has, however, a large impact on the efficiency of the simulation.

Simulated annealing is, as mentioned above, based on such a Metropolis scheme, however, during the simulation, the temperature is lowered to zero step by step. Therefore, at the beginning, parts of the configuration space with higher energies are explored, while towards the end of the simulation, the system converges towards a minimum. While there is no guarantee that the system converges to the global minimum, for small systems good results can be achieved in reasonable computer time. It is good practice to run several simulations per set of parameters to make sure a good result has been found. For the results presented in this section 16 simulations per set of parameters have been run and at the end the one which gave the lowest final energy was selected.

In the simulations discussed in this contribution, the magnetic moment of the particle is set such that the ratio of the interaction energy between two sd-particles in the optimal configuration (close contact, coaligned dipoles) and $k_B T$ is unity at the beginning of the simulation. While this is not relevant for ground states in general, in simulated annealing calculations, the energy

due to potentials has to be comparable to the initial thermal energy. Otherwise, some parts of the configuration space may not be sampled, because of too high energy barriers. In our simulations, we lower the temperature from one to zero in 200 equally sized steps. At each temperature 8×10^6 Monte Carlo moves are executed. Another 16×10^6 moves are performed at zero temperature to fine tune the solution (at zero temperature, only modifications that lower the energy further are accepted). In each move, a new configuration is proposed by slightly moving and rotating one of the particles. New positions and orientations are drawn from a Gaussian distribution centered around the previous value of the respective coordinate. During the simulation, the width of the Gaussian for obtaining new positions can be altered every 1000 moves: when more than 600 or less than 400 of the last 1000 moves got accepted, it is divided or multiplied by 1.01. In this way, at temperatures close to one, the configuration space is efficiently sampled and at lower temperatures, finer corrections are applied. The width of the distributions from which changes to the orientation are drawn, on the other hand, is kept constant at $\approx 11.5^\circ$, for simplicity.

The simulation results for the lowest energy states of clusters consisting of four to six particles are shown in Fig. 8. In the non-shifted system (depicted in the leftmost column in the figure), the ground state for all clusters larger than four particles is a ring.³⁰ Due to the appearance of a minimum at a close to anti-parallel dipole orientation with increasing shifts, discussed in the previous sections, the ground state structure in the shifted-dipole system changes noticeably. From the results for two and three particles, we conclude that pairs of dipoles with close to anti-parallel orientation and ring-like configuration are very favorable. These basic structures are also present in larger clusters. For four particles, we observe a rectangular configuration with ring-like dipole orientation for shifts α below 0.65, *i.e.*, a structure different from the one found in the non-shifted system only occurs at rather high shifts. For shifts between 0.65 and 0.675, the particles arrange in a rhombic structure. This structure can also be seen as part of a hexagonal crystal, which we find for all larger clusters at high shifts. After the transition, three dipoles form a ring while the fourth dipole moment forms a pair with

anti-parallel orientation with one of the particles of the ring. For values of $\alpha \geq 0.75$, the dipoles reorganize into an up-down-up-down configuration very similar found to the one for three particles. For a shift close to 0.75, the distance between all pairs of dipoles still is roughly the same, and thereby all pairs contribute approximately equally to the energy. When the shift is increased further, the configuration splits into two pairs of very closely neighboring dipole moments. This splitting happens, because it allows the distance between the dipole moments to be further reduced, which strongly lowers the energy.

The ground state structure for five- and six-particle clusters are also initially rings. After the transition to a close-packed structure, at intermediate shifts, the dipole configuration is composed of triangles with ring-like dipole configuration and pairs with close to anti-parallel dipole configurations.

In both of these structures, the dipoles are located very close to each other and the sum of their respective interactions with other dipoles in the system adds up to almost zero, *i.e.* the cluster only interacts very weakly with other particles. Thus, for example the energy for the five-particle cluster converges toward the sum of the energies for a pair and a triangle at high shifts, and the energy for a six-particle cluster is close to twice the energy of a triangle for intermediate shifts, and three times the energy of a pair for high shifts. On the basis of this observation, the ground state energy of larger clusters that are very difficult to obtain with simulated annealing can be estimated for intermediate and high shifts. Two different regimes have to be distinguished: when the shift is smaller than approximately 0.8, the energy per particle is lower in the triangle configuration. Thus, the number of triangles in the cluster is maximized. Let N be the number of particles, and E_3 and E_2 the energies per particle in a triangle and a pair configuration, respectively, for a fixed value of the shift. When $N \bmod 3 = 0$, the cluster consists of triangles only – the most favorable configuration with an energy per particle

$$E = E_3. \quad (7)$$

When $N \bmod 3 = 1$, the cluster consists of $(N - 4)/3$ triangles and two pairs – the most unfavorable configuration with an energy per particle

$$E = \frac{(N - 4)E_3 + 4E_2}{N}. \quad (8)$$

When $N \bmod 3 = 2$, the cluster consists of $(N - 2)/3$ triangles and a single pair. The energy per particle then is

$$E = \frac{(N - 2)E_3 + 2E_2}{N}. \quad (9)$$

When, on the other hand, for the given shift the energy per particle in a pair is more favorable, two cases have to be distinguished. When the number of particles is even, the cluster consists of pairs only, resulting in an energy per particle of

$$E = E_2. \quad (10)$$

For an odd number of particles, $N - 3$ pairs and one triangle are formed. The energy per particle is

$$E = \frac{(N - 3)E_2 + 3E_3}{N}. \quad (11)$$

Fig. 8 Lowest energy states of small clusters obtained using simulated annealing. The number next to every configuration denotes the shift value α at which the structure was observed. At low shifts, rings and chains are formed. At higher shifts, the structures become more closely packed where the dipoles take on a triangular or an anti-parallel configuration. The right most number N stands for the number of particles.

The resulting energies for clusters of 6 to 30 particles are shown in Fig. 9 for a shift of 0.55 and 0.85, respectively.

In the next figure (Fig. 10) we provide the ground state energy of 6 particles obtained in simulated annealing and compare it with the energy of 2 triangles and three sd-particle pairs. One can see that the predictions of eqn (7)–(11) work accurately in the given range of the shift values α .

At this point we would like to come back to the experimental system of ref. 43 where ground states of clusters of capped magnetic colloids were studied. The clusters containing three to seven particles always contain a triangular motif, which is also what we observe for particular shift values, see Fig. 8. However, we do not observe exactly their cluster configurations, since details of the interaction are probably different.

The authors of that study also found very stable clusters with magic numbers. For example, a cluster of twelve particles shows a very symmetric arrangement where the magnetic macrospins of the colloids are trying to reorient in such a way that they form triangular configurations, see Fig. 11a. To check if we can also obtain such a configuration we performed an additional MC simulated annealing run for a cluster composed of twelve particles the centres of which were fixed in the hexagonal lattice which corresponded to the one of the Baraban *et al.* experiment. The moments were completely free to relax to their ground state configuration. We found that a shift value of $\alpha = 0.6$, gives the closest match, see Fig. 11b. This shift fits in the range, where configuration 2 from Fig. 3 provides the ground state.

The observed qualitative agreement with the experimental data leads us to speculate that the main part of the interaction of capped colloids can be explained in terms of shifted dipoles,

Fig. 10 The ground state energy per particle obtained by simulated annealing for the system of six sd-particles is plotted in light blue triangles. The energy per particle in the system of two noninteracting triangles is plotted in red squares (middle curve). The energy of 3 noninteracting anti-parallel pairs is plotted in black squares (upper curve). For shifts $\alpha \in (0.7, 0.76)$ the ground state energy per particle of 6 sd-particles can be described by eqn (7), whereas for $\alpha > 0.85$ the energy approaches the value given by eqn (10). Here, all energies are normalized by the value $\mu_0 m^2 / (4\pi R^3)$, and the head-to-tail configuration energy is rescaled to -1 .

without even the need to include a quadrupolar part as has been done in ref. 46. However, the interaction of shifted point dipoles is probably much simpler than the one of the capped magnetic colloids, thus even though the main magnetic structures can be modeled by sd-particles, for detailed investigation of magnetic capped colloids an extension of our model might be needed. Another important fact is, that if we increase the value of the

Fig. 9 Estimate for the energy of larger clusters of sd-particles for a shift of 0.55 (plot (a), where the lowest curve corresponds to eqn (7), the middle one represents eqn (9), and the highest energy curve is obtained for clusters, where the number of particles (N) is such, that $N \bmod 3 = 1$, eqn (8) and 0.85 (plot (b), where the upper curve depicts eqn(11) and the lowest energy is reached for the clusters made of an even number of sd-particles eqn(10)), respectively. At intermediate and high shifts, clusters consist of tightly bound pair- and triangle configurations only. The interaction among different pairs and triangles is very small. Therefore, the energy of the cluster can be estimated from the energies per particle in the pair and triangle configuration for the given shift. Depending on the energy per particle for a given shift being more favorable in a triangle- (a) or pair configuration (b), different “magic numbers” arise. Here the energy, besides being calculated per particle is normalized also by the value $\mu_0 m^2 / (4\pi R^3)$.

Fig. 11 (a) Image of twelve capped colloids adapted from ref. 43, where particles form six triangles. These triangles are also drawn on top of the figure for clarity. (b) Ground state results of MC simulated annealing performed on twelve particles with fixed positions mimicking the experimental situation but freely rotating dipoles ($\alpha = 0.6$). One can see that the model of shifted dipoles indeed reproduces the magnetic structure observed for magnetic capped colloids, even though the interaction in our case is simplified.

shift α , the magnetic structuring will change, and antiparallel pairs will form. This prediction could actually be checked experimentally if magnetic caps can be produced such that their effective magnetic moment can be moved more towards the surface of the colloid, which seems experimentally feasible.⁴⁷

As a result one can conclude that the behaviour of the sd-particles at low temperature is predominantly governed by the value of the shift α . This will also affect the properties of a q2d system at room temperatures which we are exploring in the next section.

6 Larger systems at finite temperature

In the previous sections, it was shown that the ground state structures of small clusters of sd-particles are quite different from that of non-shifted-dipole particles. In this section, preliminary results for larger systems at a temperature above zero are discussed.

In Fig. 12, magnetization curves for a 400 particle system at an area fraction of 3% with periodic boundary conditions are shown for several shifts of α . Here, an external magnetic field is aligned in the layer plane. The results have been obtained by performing Monte Carlo simulations at constant temperature using the Metropolis algorithm, described in the previous section. Similar to the ground state studies, the simulations were performed in q2d geometry, *i.e.* the particles' centre of mass is fixed in the xy -plane, whereas the particles can rotate in three dimensions. The strength of the dipole-dipole interaction compared to the thermal energy was set to

$$\lambda = \frac{\mu_0 m^2}{4\pi k_B T (2R)^3} = 3$$

at a shift of $\alpha = 0$. Here, μ_0 is the vacuum permeability, m is the magnitude of the particles' dipole moment, $k_B T$ is the thermal energy and $2R$ is the particle diameter. As the lowest possible energy for two interacting sd-particles decreases quickly with increasing shift (see Fig. 2), an additional scaling was applied to keep results for different shifts comparable: at all shifts, the ratio between the energy of a single particle perfectly aligned along the

Fig. 12 Magnetization curve of a 400 particle shifted-dipole system with periodic boundary conditions at an area fraction of about 3% and an interaction parameter $\lambda = \frac{\mu_0 m^2}{4\pi k_B T (2R)^3} = 3$ for several shifts α . An external field is aligned in the layer plane. At all shifts, the ratio of both, the maximal dipole-dipole interaction between two particles and the thermal energy $\frac{U_{dd}}{k_B T}$, and the ratio of $\frac{mH}{U_{dd}}$ is kept constant. At high shifts, the magnetization of the system is hindered, because neighboring dipoles are anti-parallel aligned.

external magnetic field and the lowest possible energy of two interacting sd-particles was kept constant. This was achieved by using an effective $\lambda^*(\alpha)$ depending on the shift α :

$$\lambda^*(\alpha) = \frac{\lambda}{U_2(\alpha)/U_2(0)}, \quad (12)$$

where $U_2(\alpha)$ is the lowest possible energy for two interacting sd-particles at a shift of α .

The magnetization curve of a larger system changes strongly with increasing shift. One can argue that at higher shift particles in close proximity more often assume configurations with anti-parallel or ring-like dipole configurations rather than chains as it is typical for the non-shifted systems. Therefore the system of shifted dipoles appears to be more difficult to magnetize. The strongest difference occurs at small fields, when the microstructure is still predominantly governed by the dipole-dipole interaction. An external magnetic field of high strengths can always align the dipoles and, therefore, the influence of the shift vanishes. From the magnetization curves shown in Fig. 12, it can be seen that suspensions of shifted dipole particles show a very different local structure and different macroscopic properties. A more thorough investigation of these properties will be left for future investigations.

7 Summary

In this contribution, we studied in detail the behaviour of the model system consisting of shifted dipoles. We mainly focused our attention on the ground state structures of small clusters. In addition, preliminary results for magnetic properties of larger systems at finite temperature were discussed.

In systems of sd-particles, the local structure differs strongly from those found in non-shifted-dipole magnetic fluids: the formation of closely packed structures rather than chains and rings is enhanced by shifting the magnetic dipole from the centre of the particle towards its surface.

For two particles we observe three different ground states depending on the value of the shift α : for $\alpha < 0.408$ the head-to-tail orientation of the magnetic moments; for $\alpha \in (0.408, 0.597)$, the angles change unequally until the symmetrical anti-parallel configuration is reached; for $\alpha > 0.597$, the moments keep rotating towards each other symmetrically, so that they tend to reach an anti-parallel orientation with zero distance between them at $\alpha = 1$.

For three particles the ground state structure also changes drastically with increasing shift. There are four qualitatively different ground states depending on α : a chain for $\alpha \in (0, 0.258)$; a triangular configuration for $\alpha \in (0.258, 0.799)$; an up-down-up symmetrical configuration for $\alpha \in (0.799, 0.848)$; an asymmetric configuration at $\alpha = 0.848$, when an antiparallel pair starts to form.

The ground state structures of larger clusters, which were obtained by simulated annealing, are built up by a combination of ring-like dipole configurations – often of three particles – and pairs of two anti-parallelly oriented dipoles. At high shifts, in particular, larger clusters can almost entirely be viewed as a combination of three-particle rings and of pairs with an anti-parallel dipole orientation. For these two and three particle clusters, analytic results for the ground state configuration and energy were given, which can be used to estimate the ground state energy of larger clusters: for intermediate shifts, the energy per particle in the triangle configuration is more favorable, thus the number of triangles in the cluster is maximized, while for high shifts the pair formation is more favorable. Thus, we observe a sequence of more and less favorable cluster sizes with a period of three for intermediate, and a period of two for high shifts.

The investigations of the ground states led us to the conclusion that the shift has to influence the behaviour of bulk systems at room temperature. To this end we presented preliminary results for magnetization properties of suspensions at room temperature. In these systems, the change in local structure strongly lowers the initial susceptibility, *i.e.* the slope of the magnetization curve at zero external field.

In conclusion, the shifted-dipole system has many unexpected properties different from non-shifted system and enhances our understanding of the behaviour of dipole particles with an additional asymmetry. Undoubtedly, there are still many open questions in the description of ferrofluids with shifted dipoles. Currently we are working on the development of the theoretical description of magnetic properties of systems with shifted dipoles. Also, a detailed quantitative analysis of the cluster formation at room temperature and the study of three-dimensional systems are in progress.

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