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Self-assembly of designed supramolecular magnetic filaments of different shapes

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ABSTRACT

In the present work we study via molecular dynamics simulations filaments of ring and linear shape. Filaments are made of magnetic nanoparticles, possessing a point dipole in their centres. Particles in filaments are crosslinked in a particular way, so that the deviation of the neighbouring dipoles from the head-to-tail orientation is penalised by the bond. We show how the conformation of a single chain and ring filament changes on cooling for different lengths. We also study filament pairs, by fixing filaments at a certain distance and analysing the impact of inter-filament interaction on the equilibrium configurations. Our study opens a perspective to investigate the dispersions of filaments, both theoretically and numerically, by using effective potentials.

1. Introduction

In the last decade it has become clear that one of the leading tendencies in modern science lies in the nanotechnology, where the magnetic particles play a significant part. Such particles can vary from a few to hundreds of nanometers and are normally included into more complex material, such as liquids, gels and other carriers. Despite the fact that first stable suspensions of magnetic nanoparticles (ferrofluids, magnetic fluids) were synthesised more than 50 years ago [1], they are still not fully explored both in theory and experiments. The fact is that ferrofluids in particular, and dipolar soft matter in general, could simply modify their properties because of various external drives such as temperature changes and influence of an external magnetic field. Therefore the amount of technological, medical and even art applications of these systems is rather large and grows significantly: hyperthermia cancer-treatment therapy, loudspeakers, magnetic drug transport, contrast agents, seals, dampers, separation machines [2–5]. Magnetic nanoparticles behave as small permanent nanomagnets because of the presence of intrinsic magnetic moments. These magnets can interact with each other via the magnetic dipole-dipole interaction. If this interaction is strong enough, it leads to the self-assembly of particles in particularly shaped aggregates, like linear flexible chains, rings and networks [6–9]. Until recently it was not possible to accurately predict the formation of a certain type of aggregates under environmental changes, which led to restrictions in the applications. However, newly developed experimental techniques allowed combinations of magnetic particles and polymers, where polymer chains are grafted to the surface of a nanoparticles. These techniques make it possible to create a certain aggregated structures with finely controllable mechanical, magnetic and other properties.

We study the self-assembly properties of magnetic filaments—one of the examples of such aggregated structures—which are semiflexible polymer-like chains of magnetic nanoparticles permanently crosslinked with polymers [10–13]. We investigate two different crosslinked conformations—simple open chains and closed rings. First, we perform computer simulations to study different structural parameters of a single filament. Second, we investigate the effective interaction potentials corresponding to the equilibrium conformations of a single filament and of a pair of filaments.

This paper is organised as follows. First (Section 2) we discuss modelling approach for linear and ring magnetic filaments. In the next section (Section 3) we analyse obtained simulation data. The summary of the work and outlook are provided in Conclusion.

2. Model and methods

2.1. Model

As the first step, we consider magnetic filaments formed by monodisperse magnetic colloids. The long-range magnetic interaction between any pair of magnetic particles is described by the conventional dipole–dipole potential:

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$$U_{dd}(\vec{r}_{ij};\vec{\mu}_i,\vec{\mu}_j)=\frac{\vec{\mu}_i\cdot\vec{\mu}_j}{r^3}-\frac{3[\vec{\mu}_i\cdot\vec{r}_{ij}][\vec{\mu}_j\cdot\vec{r}_{ij}]}{r^5}, \quad (1)$$

where $\vec{\mu}_i$ and $\vec{\mu}_j$ are the dipole moments of i and j particles correspondingly, $\vec{r}_{ij}=\vec{r}_i-\vec{r}_j$ is the displacement vector connecting their centres, $r=|\vec{r}_{ij}|$. The soft core interaction between the nanoparticles is given by the Weeks–Chandler–Andersen pair potential [14]:

$$U_{\mathrm{WCA}}(r)=\begin{cases}U_{\mathrm{LJ}}(r)-U_{\mathrm{LJ}}(r_{cut}), & r<r_{\mathrm{cut}}\\ 0, & r\geq r_{\mathrm{cut}}\end{cases}, \quad (2)$$

where $U_{\mathrm{LJ}}(r)$ is the Lennard-Jones potential:

$$U_{\mathrm{LJ}}(r)=4\epsilon_s[(d/r)^{12}-(d/r)^6], \quad (3)$$

which in expression (2) has been truncated at the position of its minimum and shifted by its corresponding depth to make the resulting potential purely repulsive. The bonding effects of the crosslinkers are modelled like a simple harmonic spring whose ends are attached to the surface of the crosslinked nanoparticles. The spring attachment points are located on the surface of the particles, at a distance $d/2$ from their centres. The corresponding expression for a pair potential that links the surfaces of two ferromagnetic particles i and j is:

$$U_S(\vec{r}_{ij};\hat{\mu}_i,\hat{\mu}_j)=0.5K_S(\vec{r}_{ij}-(\hat{\mu}_i+\hat{\mu}_j)d/2)^2, \quad (4)$$

where $\hat{\mu}_i=\vec{\mu}_i/|\vec{\mu}_i|$ and $\hat{\mu}_j=\vec{\mu}_j/|\vec{\mu}_j|$ are the unitary vectors parallel to each associated dipole moment [15]. Finally, to keep the bond length finitely extensible, we also impose FENE interaction on the nearest neighbours in filaments:

$$U_{FENE}(\vec{r}_{ij})=-K_f\ln[1-(\vec{r}_{ij}/r_f)^2]/2, \quad (5)$$

where K_f is equal 30, $r_f=1.5d$. The simulations were performed with the ESPResSo 3.2.0 package [16].

2.2. Computer simulation methods

We focus on two structures: chains and rings, the sketches of which are shown in Fig. 1. In all simulations we use dimensionless parameters, taking as reference the reduced characteristic diameter and mass of the magnetic nanoparticles, d=1 and m=1 respectively, and the prefactor of the reduced soft core potential (2), $\epsilon_s=1$, to which also the reduced temperature T is normalised. The values taken for the interparticle interaction parameters are $K_s=30$ for the prefactor of the potential (4). These parameters give average bond lengths close to the characteristic diameter of the bead soft core, d=1, and a maximum distance between two bonded particle surfaces not larger than half of such diameter. These choices correspond approximately to, for example, magnetite spherical particles with a magnetic core diameter of approximately 25–30 nm and a 5–10 nm polymer coating, which is also used to crosslink the particles.

The evolution of the filament chain conformation can be characterised by two following parameters. Firstly, we compute the total dipole moment of the filament chain made of N identical particles with the modulus of dipole moment μ

$$M=\frac{1}{N\mu}\left|\sum_{i=1}^{N}\vec{\mu}_i\right|. \quad (6)$$

Secondly, the radius of gyration can be measured

$$R_g^2=\frac{1}{N}\sum_{i=1}^{N}(\vec{r}_i-\vec{R}_{cm})^2, \quad (7)$$

where r_i is the position of the centre of particle i, R_{cm} is the position of a filament centre of mass. This value for a perfect ring coincides with its geometrical centre and for an ideal rod structure with its middle point. However, in thermodynamic equilibrium, the centre of mass of a filament can move depending on the conformation. The observable R_g can also be used to characterise the evolution of ring filaments. In order to investigate the properties of a single filament, be that a chain or a ring, we used parallel tempering [17]. The dipole moment of each particle was fixed at $\mu^2=3;5;8$, the number of particles in a filament was $N=10;20;30$. The temperature range $T\in[0.3,6.5]$. We used molecular dynamics simulations with a Langevin thermostat, in combination with the replica exchange method. The latter was used to avoid the system to get trapped into a local minimum. The study of two filament interaction was performed via simple molecular dynamics simulation with a Langevin thermostat. We fixed central particles of two filaments (in case of a ring, without loss of generality, the first particle was fixed) at a given distance, equilibrating the system. After equilibration we were evaluating the distance between filament centres of mass δR_{cm}. Note that δR_{cm} can change even though one particle in each filament is fixed. We varied the distance between fixed particles from one particle diameter to 17 particle diameters. This corresponded to the maximum separation between the centre of masses of approximately 15.

3. Results

In this section we provide the main results for single and two filament configurations at various temperature, dipolar strength and inter-filament distance.

3.1. Single filament

In Fig. 2a, we show how the total magnetic moment of a filament changes with temperature. In the upper row, we plot the data for chains, whereas in the lower row, the analogous data is plotted for the ring filament. From the left to the right the size of the filament grows. For an ideal straight chain the value should be equal to unity; for an ideal ring $\langle M\rangle=0$. These values are never reached, which, on the one hand, evidences the influence of the thermal fluctuations. On the other hand, for chain filaments, the total magnetic moment grows on cooling, but then drops abruptly. The latter can be explained by the closing transition: the chain closes into a ring. In Fig. 2b it is confirmed by temperature dependence of R_g. Besides, if one looks at the end-to-end distance for chain filaments (we provide no figure for R due to the lack of space), it undergoes the same evolution, first growing and then

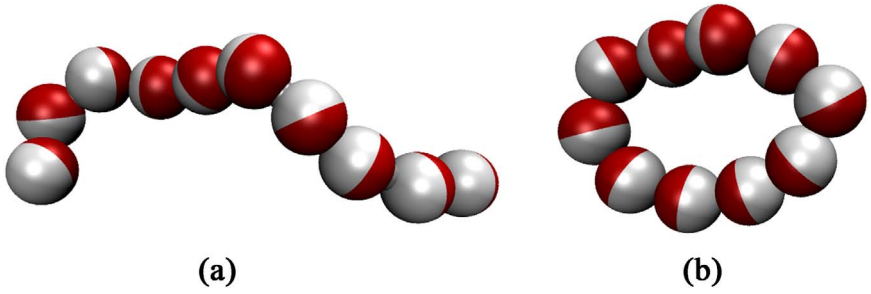

Fig. 1. A chain and a ring filament configurations, coloured hemispheres indicate the orientation of the magnetic moments. (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this paper.)