# Effects of the dipolar interaction on the equilibrium morphologies of a single supramolecular magnetic filament in bulk

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We study the equilibrium morphologies of a single supramolecular magnetic filament in a three-dimensional system as a function of the effective strength of the magnetic dipolar interactions. The study is performed by means of Langevin dynamics simulations with a bead-spring chain model of freely rotating dipoles. We demonstrate the existence of three structural regimes as the value of the dipolar coupling parameter is increased: a coil compaction regime, a coil expansion regime and a closed chain regime in which the structures tend progressively to an ideal ring configuration. We discuss the governing effects of each regime, the structural transition between open and closed morphologies, and the reasons why we see no multiloop configurations that have been observed in two-dimensional systems under similar conditions.

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## I. INTRODUCTION

Supramolecular magnetic filaments are assemblies of nanometer sized magnetic particles linked by polymers or other molecules to form a chain. These systems are the basis of a novel nanotechnology that combines in a unique way the interesting physical properties of magnetic nanoparticles (MNPs) with the intrinsic anisotropies of one-dimensional semiflexible chains<sup>1</sup>.

Research on MNPs has become an extremely active field in recent years<sup>2–5</sup>. In particular, the self-assembly of MNPs into stable structures, mainly governed by dipolar interactions, is a topic of great interest. The zero-field self-assembly of magnetic colloids into dipolar rings —with the individual magnetic moments disposed in a head-to-tail arrangement along the chain— was predicted more than four decades ago<sup>6</sup> and since then has been extensively studied by means of theoretical models and simulations<sup>7–14</sup>. However, the first experimental observations of self-assembled chains of MNPs are more recent and, in late years, have led to the finding of different self-assembled structures of two-dimensional dispersions of dipolar chains, including flux closure structures like rings, necklaces or other two-dimensional multiloop configurations<sup>15–24</sup>. The direct observation of closed ring-like structures in three-dimensional dispersions of MNPs is experimentally challenging, but their existence has been predicted theoretically by means of different simulation models<sup>20,25–27</sup>.

On the other hand, research on magnetic filaments is rather scarce. After the seminal works reported in the late 1990s for the assembly of micrometer sized particles<sup>28,29</sup>, the progress in synthesis methods to produce them has allowed the preparation of magnetic filaments made of particles of very different materials and characteristic sizes<sup>30–37</sup>. In addition, the filaments can now be made much more flexible, a property which is mainly determined by the nature of the molecular links between the MNPs and, to some extent, by the intensity of their magnetic interactions. So far, most studies on single or highly diluted magnetic filaments in bulk have been restricted to the understanding of their dynamic properties under the action of external magnetic fields, paying a special attention to their application as nanofluidic propellers and actuators<sup>22,32,37–43</sup>. The equilibrium configurational properties of the filaments have been generally disregarded. Nevertheless, the chain morphology has been pointed out as a relevant factor for some properties of the filaments that are of high interest like its thermal and electric conductivity or its overall coercivity<sup>1</sup>.

As a general hypothesis, it is reasonable to expect that the configurations observed in

self-assembled chains of MNPs may appear also as equilibrium morphologies of magnetic filaments with an adequate degree of flexibility. Nevertheless, it is not obvious which conditions may lead to the different equilibrium structures or what will be the behavior of the filaments under conditions which do not lead to the self-assembly of free particles into dipolar chains. Therefore, the chain connectivity imposed by the chemical links makes magnetic filaments a system with a structural behavior that is expected to be clearly distinguishable from the corresponding to assemblies of free particles. In addition, there is still little knowledge on the equilibrium structures of either highly diluted self-assembled dipolar chains and magnetic filaments in bulk.

In a recent work<sup>44</sup> we introduced a simple coarse-grained simulation model for the study of the equilibrium behavior of semiflexible magnetic filaments near an attractive flat surface. We reported the effect of the dipolar interactions on the adsorption transition and the existence of different equilibrium morphologies that depend on the temperature and the magnetic dipole strength. In particular, we found different adsorbed closed chain structures, ranging from simple rings to more complex two-dimensional closed configurations in which not only the ends but also some middle points of the chain become in close contact to form a number of small linked rings. Such simple rings and multiloop structures are very similar to the ones found in the most recent experimental observations of self-assembled chains of magnetic nanoparticles<sup>33,45</sup>.

In the present work we explore the corresponding equilibrium morphologies of magnetic filaments in the bulk using our previously introduced model. In particular, we intend here to qualitatively determine the effects of the magnetic interactions on the local and global configurations of a fully flexible dipolar chain without the geometrical constrains imposed by the presence of an adsorbing surface.

The work is organized as follows: in Section II we review the details of the proposed model and the simulation method, in Section III we present and discuss the results of our simulations and we end with the concluding remarks in Section IV.

## II. SIMULATION MODEL AND METHOD

In order to explore the equilibrium behavior of a magnetic filament in bulk we have taken just the required ingredients from our previous coarse-grained model<sup>44</sup>: the linking potential, the dipolar interaction and the steric repulsion between the beads. Therefore, in our model a magnetic filament is represented as a bead-spring chain of N identical particles carrying at their centers a point magnetic dipole,  $\vec{\mu}$ , which can freely rotate in any direction.

It is important to remark that in our model the free rotation of the dipoles is just a computational simplification useful for dynamical simulations. In experimental chains of ferromagnetic particles the molecular links tend to prevent the rotation of the particles and, therefore, the reorientation of their respective dipoles. The natural disposition of such chains is a permanent head-to-tail alignment of the dipoles with respect to the chain backbone. The head-to-tail alignment is also found experimentally for chains of superparamagnetic particles as a consequence of a cooperative effect: the increase of the dipole reversal barriers in every bead led by the external field generated by its neighbors<sup>46</sup>. Nevertheless, according to what we observed in our previous studies with this model<sup>44</sup>, we expect that a spontaneous head-to-tail alignment will be observed for large enough values of the dipole moment without imposing any explicit constraint to the reorientation of the dipoles. The drawback of this approach is that we should expect the existence of a region of relatively weak dipolar interactions—either led by a low value of the dipole moments and/or by a high system temperature—in which the alignment will not take place and the model will not be representative of a ferromagnetic behavior.

The details of our model are the following: the steric repulsions between the beads are modeled by means of a Weeks-Chandler-Andersen potential (WCA)<sup>47</sup>:

$$U_{\rm WCA}(r) = \begin{cases} U_{\rm LJ}(r) - U_{\rm LJ}(r_{cut}), \ r < r_{\rm cut} \\ 0, \qquad r \ge r_{\rm cut} \end{cases},$$
(1)

where r is the distance between the centers of the interacting beads,  $U_{\rm LJ}(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6]$  is the standard Lennard-Jones potential,  $r_{\rm cut} = 2^{1/6}\sigma$  is the shifting parameter selected to make the potential repulsive and  $\sigma$  is the characteristic diameter of the beads. Typically, the range of experimental values of  $\sigma$  varies between 10 and 200nm. The bonds between adjacent beads in the chain are formed by means of a finite extensible non linear elastic potential (FENE), defined as:

$$U_{\text{FENE}}(r) = \frac{-K_f r_{\text{max}}^2}{2} \ln\left[1 - \left(\frac{r}{r_{\text{max}}}\right)^2\right],\tag{2}$$

with  $K_f = 30/\sigma^2$ , and  $r_{\text{max}} = 1.5\sigma$ . The use of this potential implies to have the linking springs attached to the center of the beads, therefore neglecting the eventual bond stretching

produced by rotations of the linked particles. The long-range magnetic interactions are represented by the conventional point dipole-dipole potential

$$U_{\rm DIP}(\vec{r}_{ij};\vec{\mu}_i,\vec{\mu}_j) = \frac{\vec{\mu}_i \cdot \vec{\mu}_j}{|\vec{r}_{ij}|^3} - \frac{3\left[\vec{\mu}_i \cdot \vec{r}_{ij}\right]\left[\vec{\mu}_j \cdot \vec{r}_{ij}\right]}{|\vec{r}_{ij}|^5},\tag{3}$$

where  $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$  is the displacement vector between the centers of the beads *i*, *j* and  $\vec{\mu}_i$ ,  $\vec{\mu}_j$  are the dipole moments associated to each bead. For spherical particles forming a ferromagnetic monodomain  $\mu$  is related to the intrinsic magnetization of the material,  $M_S$ , and the particle diameter,  $\sigma$ , as  $\mu = \frac{1}{6}\pi\sigma^3 M_S$ . Section I of the Supplemental Material of this article<sup>48</sup> includes a plot with the different potentials defined in our model.

In magnetic dipolar systems it is usual to define a dimensionless dipolar coupling parameter,  $\lambda$ , to represent the effective intensity of the dipolar interactions. For a system of identical dipolar spheres, this parameter is commonly defined as the ratio between the optimum magnetic energy of two dipoles—corresponding to a close contact in a head-to-tail arrangement— and the thermal fluctuations:  $\lambda = \mu_e^2/(kTb^3)$ , where  $\mu_e^2$  is the experimental squared dipolar moment of the spheres, k is the Boltzmann constant, T the experimental temperature and b is the characteristic separation distance between the dipoles. Typically, b is the diameter of the beads or, equivalently, the distance between first-nearest neighbors in chain-like systems. Therefore, b is expected to be similar to the particle diameter parameterized in our interaction potentials,  $b \sim \sigma$ . We can take reduced units for the experimental sprameters by defining  $\mu^2 \equiv \mu_e^2/\epsilon_e$  and  $T^* \equiv kT/\epsilon_e$ , where  $\epsilon_e$  is the characteristic experimental strength of the pair interactions in our system. Therefore, we get the following expression for the dipolar coupling parameter:

$$\lambda = \mu^2 / \left( T^* b^3 \right). \tag{4}$$

We assume the qualitative equivalence of the variation of  $\mu^2$  or  $T^*$  as a reasonable approximation for the description of the equilibrium morphologies of a filament under not too extreme conditions. This assumption has been proven to be useful for the characterization of other magnetic systems like ferrofluids. Thus, we have chosen to sample  $\lambda$  by taking different values of the squared dipolar moment within a moderate range,  $\mu^2 \in [0, 20]$ , at a constant reduced temperature,  $T^* = 1$ . However, the dependence of  $\lambda$  on b prevents in our model to sample this parameter in a straightforward way. In particular, we have a bounded but not fixed distance between first-nearest neighbors in the chain. We expect such distance to depend, at least, on either the value of  $\mu^2$  or the local degree of head-to-tail alignment of the dipoles. This latter dependence makes the exact value of b unknown beforehand for any simulation we could attempt, so we can not set  $\lambda$  directly as a running dipolar parameter. On the other hand, it is very convenient to express our results in terms of  $\lambda$  in order to facilitate the comparison with previous studies. Thus we have taken  $\mu^2$  as the running dipolar parameter of our simulations and calculated the corresponding values of  $\lambda$  by applying Equation (4), with b being the measured average distance between the first-nearest neighbors in our simulated equilibrium configurations. Finally, for each selected value of the running dipolar parameter, four different chain lengths,  $N = \{10, 25, 50, 100\}$ , have been sampled.

Our simulations have been performed by means of molecular dynamics employing a Langevin thermostat in order to implicitly include the effects of the thermal fluctuations of the solvent. According to the selected reduced units, in our dynamical simulations the reduced time,  $t^*$ , is related to the experimental time, t, by  $t^* = t\sqrt{\epsilon_e/(M\sigma^2)}$ . In the following we provide the parameters used in our simulations. The common details of the simulation method can be found in Section II of the Supplemental Material<sup>48</sup>. In general, in a dynamical simulation the values of the mass, M, the inertia tensor, I, and the translational and rotational friction constants,  $\Gamma_T$  and  $\Gamma_R$ , are irrelevant for the results associated to an equilibrium state. For simplicity, we have taken  $\sigma = 1$ ,  $\epsilon = \epsilon_e = 1$ , M = 1 and the identity matrix for the inertia tensor in order to ensure isotropic rotations. For the friction constants we have taken  $\Gamma_T = 1, \Gamma_R = 3/4$ , since these values are known to produce a fast relaxation to equilibrium for dipolar systems<sup>11,12</sup>. In order to enhance the statistics and avoid the sampling overhead associated to eventual metastable configurations—which are likely to appear at high values of  $\lambda$ —we have applied the replica exchange molecular dynamics method (REMD)<sup>49,50</sup> to our Langevin dynamics simulations. In particular, we used  $\mu^2$  as the replica parameter, with a set of 66 values in the range  $\mu^2 \in [0, 20]$ . These values have been selected by requiring an exchange rate above 35% for all replicas and chain lengths. We used open boundaries and an integration time step of  $\delta t = 0.001$ . At each simulation cycle, we performed  $3 \cdot 10^6$  equilibration steps followed by  $2 \cdot 10^6$  further steps for measurements. A total of 800 cycles have been performed, but only the measures collected in the last 300 cycles have been used in our statistics. As a last remark on the simulation method, the limitation of our study to a single filament has made the direct summation the method of choice for the calculation of the long-range dipolar interactions. The simulations have been carried out using the coarse-grained simulation package ESPResSo  $3.0.2^{51}$ .

# III. RESULTS AND DISCUSSION

In order to present our results in terms of the dipolar coupling parameter,  $\lambda$ , as defined in equation 4, the first property to be determined from the equilibrated filament configurations is the average distance between the first-nearest neighbors, or mean bond length  $\langle b \rangle$ , as a function of the running dipolar parameter—the squared dipole moment,  $\mu^2$ —and the chain length, N. Figure 1 shows the values of  $\langle b \rangle$  obtained for every selected chain length along with the corresponding bond length of a dimer—i.e., a chain formed by just two dipoles which is the minimal conceivable conformation in this system. As expected, for all the cases studied,  $\langle b \rangle$  decreases smoothly with increasing strength of the dipole moment. On the other hand, the chain length has a significant impact just for the shortest chains at high dipole moments, for which the observed decrease of  $\langle b \rangle$  is lower. For longer chains, the change of  $\langle b \rangle$  is almost independent of N. The correct interpretation of this effect requires a complete understanding of the arrangement of the dipoles in the chain as  $\mu^2$ , and consequently  $\lambda$ , are increased. Such discussion is placed in Section III C. Finally, once the dependence of  $\lambda$  on  $\langle b \rangle$  has been numerically established for each selected value of  $\mu^2$  and N, we can express all



FIG. 1. Mean bond length,  $\langle b \rangle$ , as a function of the squared dipole moment,  $\mu^2$ , for different filament lengths. Error bars are smaller than symbols.



FIG. 2. Selected snapshots of equilibrium configurations obtained for different values of the dipolar coupling parameter,  $\lambda$ , and chain lengths, N. The magnetic beads are represented as two-color spheres, with dark/light colors indicating the orientation of the associated dipole. The spheres at the chain ends have a different dark color to be easily identified within the closed morphologies. For the case of the lowest value of  $\lambda$ , the scale of a region of the chain has been increased for a better observation of the clustering and disordered orientation of the dipoles.

our results in terms of  $\lambda$ .

A direct inspection of the equilibrium morphologies obtained in our simulations confirms the expectation discussed in Section II about the head-to-tail alignment of the dipoles, as well as the existence of important structural changes with the effective intensity of the dipolar interactions. Figure 2 illustrates these changes for some selected values of  $\lambda$  and N. In general, for low values of  $\lambda$  the chains show a shape similar to a swollen random coil, with a high disorder in the orientations of the dipoles. As  $\lambda$  increases, the dipoles tend effectively to align with the chain backbone in a head-to-tail configuration, while the backbone becomes more straight. At even larger values of  $\lambda$ , the chains adopt an irregular ring-like closed structure, with their ends becoming permanently in close contact. Finally, these ring-like morphologies tend to reduce their irregularities as  $\lambda$  is further increased. Shorter chains apparently show less backbone irregularities at high values of  $\lambda$ , getting closer to the twodimensional symmetry of an ideal ring. The rest of Section III is devoted to the formal analysis of these qualitative observations by means of different structural parameters.



FIG. 3. (a) Scaled mean squared value of the end-to-end distance (upper panel) and radius of gyration (middle and lower panels), as a function of the dipolar coupling parameter,  $\lambda$ , for different chain lengths. The scaling shown in the upper and middle panels corresponds to the behavior expected for a self-avoiding walk,  $\langle R_g^2 \rangle \propto N^{6/5}$ . The scaling in the lower panel corresponds to the ideal ring behavior,  $\langle R_g^2 \rangle \propto N^2$ , represented by the solid line. (b) Probability histograms of  $\langle R_e^2 \rangle / N^{6/5}$  obtained for N = 100 and some selected values of  $\lambda$ . (c) Corresponding probability histograms for  $\langle R_g^2 \rangle / N^{6/5}$ .

### A. Characteristic equilibrium structures

The squared radius of gyration,  $R_g^2$ , and end-to-end distance,  $R_e^2$ , are useful parameters for the characterization of the global shape of chain-like structures. Figure 3(a) shows the variation of the scaled mean value of such parameters as a function of  $\lambda$ . Some selected examples of their probability distributions are also shown in Figures 3(b) and 3(c). Two scaling relationships  $\langle R_g^2 \rangle \propto N^{2\nu}$  have been assumed in the representation of the data in Figure 3(a): the upper and middle panels show the values of  $\langle R_e^2 \rangle$  and  $\langle R_g^2 \rangle$  scaled with the exponent  $2\nu = 6/5$ . This exponent corresponds to an ideal self-avoiding walk, which is the expected behavior for this system in the limit  $\lambda \to 0$ . The lower panel of Figure 3(a) shows  $\langle R_g^2 \rangle$  scaled with the exponent  $2\nu = 2$ , that corresponds to an ideal ring structure expected for  $\lambda \gg 1$ . We can observe that the curves tend to collapse at different regions according to each scaling behavior:  $2\nu \to 6/5$  at low  $\lambda$  values and  $2\nu \to 2$  at large  $\lambda$ . However, it is remarkable that a perfect fit has not been reached in any case. This result indicates that the system is far from an ideal behavior, specially in the limit of large  $\lambda$  values.

Independently of the scaling applied to the data, the results shown in Figure 3 clearly indicate the existence of three different regimes and a transition-like structural change within the explored range of parameters: for  $\lambda \lesssim 2$  the chain structures tend to compact slightly with  $\lambda$ , an effect that increases with the chain length. For  $2 \leq \lambda \leq 6$  this tendency is reversed, with a significant expansion of the structures until a maximum of the overall extension is reached. At  $\lambda \sim 6$  the chain overall extension experiences a remarkable drop, with the end-to-end distance falling to its minimum equilibrium value, corresponding to the close contact separation between two non-bonded, head-to-tail oriented particles. In addition, the corresponding probability distributions show the existence of notably bigger fluctuations of both structural parameters in this region. This important change corresponds to the structural closure transition that leads to the ring-like morphologies pointed above. Finally, for  $\lambda \gtrsim 6$  the end-to-end distance remains in its minimum value, showing almost a delta function in its probability distribution, and the radius of gyration tends monotonically to a plateau. The value of this plateau is slightly lower than the corresponding to an ideal ring formed by N beads of effective diameter  $b, R_{g, ring}^2 = b^2/[4\sin^2(\pi/N)] \sim [Nb/(2\pi)]^2$ . It is also remarkable that the tendency to the plateau and its similarity to the value expected for an ideal ring are significantly lower for the longest chains. As an example, for N = 10and  $\lambda \approx 30.39$  the mean squared radius of gyration measured for our equilibrium structures is  $\langle R_g^2 \rangle \approx 1.92$ , while an equivalent ideal ring would have  $R_{g, ring}^2 \approx 1.95$ . On the other hand, for N = 100 and  $\lambda \approx 30.79$  we have measured  $\langle R_q^2 \rangle \approx 139.25$  in front of the ideal value  $R_{g, ring}^2 \approx 186.88$ . Therefore, the difference between the measured and the ideal values for



FIG. 4. Dependence with  $\lambda$  of the fitted exponent,  $2\nu$ , corresponding to the scaling relation for the average squared radius of gyration with respect to the chain length,  $\langle R_g^2 \rangle \propto N^{2\nu}$  (main plot). The inset shows how the values of  $\langle R_g^2 \rangle$  measured for  $\lambda = 0$  (data points) deviate from the ideal scaling, given by  $2\nu = 6/5$  (solid line).

 $R_g^2$  at  $\lambda \sim 30$  is of the order of 10% for N = 10 and 25% for N = 100. This effect will be better illustrated in Section III C.

The strong dependence of the closed structures with the chain length discussed above explains the deviation with respect to the ideal scaling behavior for large values of  $\lambda$  that has been observed in Figure 3(a). The deviation corresponding to small values of  $\lambda$  is, instead, a consequence of being not yet in the asymptotic scaling regime. This effect can be evidenced by fitting the scaling exponent  $2\nu$  to the available data. In Figure 4 we have represented the fitted exponent as a function of the dipolar coupling parameter. The fit has been performed by using all the simulated chain lengths. The result is qualitatively consistent with the theoretical expectations: we can observe that the value of  $2\nu$  is effectively bounded by the values corresponding to the Flory exponent for the three-dimensional swollen random coil,  $2\nu = 6/5$ , and the ideal ring,  $2\nu = 2$ . The local peak observed at  $\lambda \sim 6$  corresponds to the maximum expansion of the chain prior to the closure transition. However, the inset of Figure 4 evidences that the exponent fitted for  $\lambda = 0$  is slightly higher than the theoretical value due to the fact that we have not yet reached the asymptotic scaling regime in our sampling. An accurate estimation of the scaling exponent for the limit  $\lambda \to 0$  would require the simulation of much longer chains. Another general effect of the dipolar interactions on the chains is to make the backbone locally more straight as  $\lambda$  is increased, apparently in a rather independent way with respect to the global structure. This magnetically driven decrease of the backbone local curvature is similar to the effect led by the chain stiffness associated to bond bending potentials<sup>44</sup>. Nevertheless, it is important to keep in mind that the dipolar interactions are not strictly local as is the case of the bond stiffness. In other chain-like systems governed by long-ranged interactions—like, for example, in polyelectrolyte systems—the effects of the intensity of such interactions on the local structure of the chain are usually studied by means of the persistence length<sup>52,53</sup>. In our case, however, the existence of a closure transition led by the dipolar interactions introduces a non-local dependence of this parameter (for a discussion on the locality of the persistence length see for instance ref.<sup>54</sup> and references therein). Therefore, we choose to analyze a simple but representative local parameter: the cosine bond angle distribution. This is defined as the probability distribution of the vector product of adjacent unitary bond vectors for every position *i* along the chain:

$$C_{i} = \hat{b}_{i-1,i} \cdot \hat{b}_{i,i+1}, \tag{5}$$

where  $\hat{b}_{i,j}$  is the unitary vector pointing in the direction from the center of bead *i* to the center of bead *j*. Figure 5 shows the distributions for the cases  $N = \{10, 100\}$  corresponding to some selected values of the dipolar coupling parameter. The results show a continuous change with  $\lambda$  from an almost flat distribution, with a wide domain of values for  $C_i$ , to a distribution that progressively approaches a delta function at the point corresponding to an ideal ring:

$$C_i(\lambda \gg 1) \to \delta[\cos(2\pi/N)].$$
 (6)

The almost flat distribution observed at low values of  $\lambda$  indicates an insignificant correlation between adjacent bond vectors. For high values of  $\lambda$  the adjacent bond vectors are highly correlated, as this corresponds to a locally straight backbone. In all cases  $C_i$  is unable to take values far below -0.5 as a direct consequence of the steric repulsions.

In Sections III B and III C we analyze in more detail the structural properties found for low and high values of  $\lambda$ , respectively.



FIG. 5. Probability distributions of the cosine bond angle parameter corresponding to N = 10 (left) and N = 100 (right) obtained for different values of the dipolar coupling parameter.

#### B. Properties of open structures

We have shown that two different regimes are found for open structures. In order to understand these regimes and determine at which point the model becomes representative of a ferromagnetic behavior, we have analyzed in the first place the degree of alignment of the dipoles with the chain backbone. This alignment can be easily calculated by means of the bond-dipole alignment modulus, A, defined as<sup>44</sup>:

$$A = \frac{1}{N-2} \sum_{i=2}^{N-1} \left| \hat{b}_{i-1,i+1} \cdot \hat{\mu}_i \right|,$$
(7)

where  $\hat{\mu}_i$  is a unit vector parallel to the dipolar moment of bead *i* and  $\hat{b}_{i-1,i+1}$  is the unit vector parallel to the displacement vector between the centers of the beads i - 1 and i + 1. We expect that for any given equilibrium configuration found in our system this simple parameter will take values from 1/2 to 1. The value 1/2 corresponds to a distribution of dipole orientations completely uncorrelated with the chain backbone, whereas the value 1 is associated to a configuration in which all dipoles are perfectly aligned with it. Figure 6 shows the average and fluctuations of this parameter as a function of  $\lambda$  for every chain length. From a fully uncorrelated state at  $\lambda = 0$ , the alignment of the dipoles grows quickly with  $\lambda$  up to  $\langle A \rangle \sim 0.95$  at  $\lambda \sim 5$ , to smoothly approach to its maximum value  $\langle A \rangle = 1$ afterwords. For all cases, the fluctuations show an absolute maximum at around  $\lambda \sim 1.6$ ,



FIG. 6. Average bond-dipole alignment modulus,  $\langle A \rangle$ , as a function of the dipolar coupling parameter for different chain lengths. Its corresponding fluctuations for low values of  $\lambda$ , scaled according to the sampling statistics, are shown in the inset.

but neither the average nor the fluctuations exhibit any significant dependence on the chain length. Interestingly, the maximum in the fluctuations corresponds quite well with the minima found for  $R_g^2$  and  $R_e^2$  that separate the two behaviors associated to open structures. We conclude that a compaction or an expansion of the open chains is obtained depending on the degree of alignment of the dipoles with the chain backbone. In particular, disordered dipoles tend to favor the chain compaction by increasing their lateral contacts and allowing the formation of small, disordered and weakly interacting three-dimensional clusters, like the ones that can be observed in Figure 2 for the lowest value of  $\lambda$ . Such disordered aggregates should reduce the overall extension of the chain. The monotonous decrease of the bond length with  $\lambda$  may help slightly to the overall compaction in this region, but its impact can be neglected in front of the variations of the lateral contacts. An estimation of the number of energetically and entropically favorable lateral contacts, obtained by applying the criteria established for the aggregation of magnetic particles in ferrofluids<sup>55</sup>, supports this conclusion. The details of such estimation can be found in Section III of the Supplemental Material<sup>48</sup>.

The analysis of  $\langle A \rangle$  suggests that our free rotating dipoles tend to display a ferromagnetic behavior for  $\lambda > 3$ , where the bond dipole alignment fluctuations drop almost to zero, independently of the chain length. This limiting value can be reasonably identified with the well known condition for the self-assembly of spherical MNPs into dipolar head-to-tail chains<sup>6,17,56–59</sup>. Such condition simply reflects the fact that thermal fluctuations should be less significant than the magnetic energy of two head-to-tail aligned dipoles in order to allow the formation of a stable dipolar-driven aggregate. In our case, the bonds keep the chain connectivity even at the entropically dominated region  $\lambda < 3$ , but under such condition the dipoles are unable to remain persistently aligned and rotate like free particles. It is for  $\lambda > 3$ when the head-to-tail alignment becomes stable and the chains tend to be more straight as the alignment increases. In summary, the behavior of the open structures is mainly the result of the interplay between the thermal fluctuations and the dipolar interactions, both acting at a relatively short scale around each particle.

## C. Closure transition and properties of closed structures

The inspection of the configurations and the behavior of the radius of gyration and the end-to-end distance has evidenced the existence of a closure transition in the bulk similar to the one observed for chains adsorbed on a flat substrate<sup>44</sup>. It is known that the dipolar energy of a chain of N > 4 dipoles disposed into a head-to-tail closed ring is lower than the corresponding to a head-to-tail straight arrangement of the same length<sup>60</sup>. In particular, for N > 4, the decrease of the dipolar energy led by the added head-to-tail close contact between the chain ends overcomes the effect of the misalignments introduced by the ring curvature. On the other hand, a closed chain structure has a lower configurational entropy than an open one. Therefore, the closure transition separates the region of configurations dominated by entropy, corresponding to the open chain structures, from the energy-dominated region of the closed structures.

In order to analyze in more detail the closure transition of our equilibrium structures, we have chosen the total magnetization of the chain, M, as the characteristic parameter. M is simply defined as the module of the sum of the unit dipolar moment vectors along the chain:

$$M = \left\| \sum_{i=1}^{N} \hat{\mu}_i \right\|.$$
(8)

The behavior of this parameter is expected to be qualitatively very similar to the one observed for the end-to-end distance<sup>44</sup>, but the accurate estimation of the fluctuations of Mis found to be easier than the corresponding to  $R_e^2$ . Figure 7 represents the relative mean value of M and its fluctuations. Initially, M grows with  $\lambda$  up to a maximum value, from



FIG. 7. Mean total magnetization as a function of the dipolar coupling parameter for different chain lengths and its corresponding fluctuations (inset).

which a sudden drop to almost zero is observed around  $\lambda \sim 6$ . For higher values of  $\lambda$  it remains persistently close to zero. The almost zero value of M indicates that the magnetic flux along the chain is following a nearly closed trajectory, as corresponds to a closed structure of head-to-tail aligned dipoles. Remarkably, the fluctuations of M, shown in the inset of Figure 7, display clear peaks indicating the position of the transition points,  $\lambda_0$ . These transition points shift to higher values of the dipolar coupling parameter as the chain length increases: from  $\lambda_0 \sim 5.5$  for N = 10 to  $\lambda_0 \sim 6.5$  for N = 100. These closure points are consistent with the structural phase diagram known for low density dispersions of free MNPs<sup>61</sup>. However, it is well known that self-assembled structures of free MNPs tend to be quite heterogeneous, with a coexistence of open and closed structures in a wide range of parameters. This heterogeneity is not limited to experimental observations—in which other more complex short ranged interactions, hard to control and predict, might play an important role—but is also found in simulations with other minimalistic models similar to ours. Therefore, the self-assembly of free magnetic particles does not represent a structural transition. This makes a significant difference with our dipolar chains, for which the chain connectivity leads to a well defined transition-like behavior.

We have seen that for  $\lambda > \lambda_0$  the chains remain in a closed configuration, but it is left to determine how far they are from an ideal ring configuration. This can be characterized by means of different shape parameters calculated from the average principal moments of



FIG. 8. Shape parameters of the chains for every sampled value of  $\lambda$  and N. These shape parameters are defined as the ratios of the average principal moments of the gyration tensor:  $L_2/L_1$  (upper panel) and  $L_3/L_1$  (lower panel).

the gyration tensor of the sampled configurations,  $L_1 \ge L_2 \ge L_3$ . Here we choose to analyze the ratios of the average second and third moments to the first one,  $L_2/L_1$  and  $L_3/L_1$  respectively. Figure 8 shows the behavior of these parameters with  $\lambda$  for every chain length. For  $\lambda = 0$  we can observe that our measures are in good agreement with the ratios corresponding to the shape anisotropy of a swollen random  $\operatorname{coil}^{62}$ ,  $L_1 : L_2 : L_3 \approx 12 : 3 : 1$ . For  $\lambda \gg 1$ , the shape parameters tend to  $L_2/L_1 \to 1$  and  $L_3/L_1 \to 0$ , values that correspond to the ideal ring. This result evidences the tendency to approach an ideal ring structure as  $\lambda$  increases. The strong dependence of this tendency on the chain length also evidences that the ideal ring is more difficult to achieve for the longest chains. At values of  $\lambda$  in the vicinity of the closure transition point  $\lambda_0$ , the behaviour is rather complex and strongly dependent on the chain length. In particular, for  $\lambda \gtrsim \lambda_0$  a monotonic increase of  $L_2/L_1$  can be observed for chain lengths N < 100. For N = 100, instead, there exists an interval just above  $\lambda_0$  in which  $L_2/L_1$  slightly decreases, indicating an slight increase of the eccentricity of the closed chain in the plane of its first two principal axes. This suggest that further structural regimes with different shape anisotropies may appear as the chain length increases. An adequate characterization of such eventual new regimes will require the exploration of a wider range of chain lengths.

At the beginning of Section III we provided an evidence of a significant impact of the

chain length on the average bond length,  $\langle b \rangle$ , mainly for short chains and strong dipolar interactions (see Figure 1). This behavior can be explained by the interplay between the dipolar interaction that every particle experiences with second and further nearest neighbors in the chain and the local curvature imposed by the ring-like structures found for strong dipolar interactions: on one hand, dipolar interactions with further nearest neighbors are only significant for high dipolar moments and a good head-to-tail alignment with such close neighbors. Under these conditions, the bonding potential well between first nearest neighbors is shifted to a shorter equilibrium distance (see Figure 1 in the Supplemental Material<sup>48</sup>). However, only long enough chains are able to keep a high local curvature—i.e., a good alignment between further nearest neighbors—when they form a ring-like structure at high values of  $\lambda$ . Instead, this effect of non-first nearest neighbors is hindered by the increased misalignment led by a shorter chain ring.

Finally, and as a difference with previous results on magnetic filaments adsorbed onto a planar surface<sup>44</sup>, we found no trace of two-dimensional multiloop structures in the bulk. Smooth two-dimensional multiloop structures can be slightly more energetically favorable than a single ideal ring, provided they keep the closed head-to-tail contact between the chain ends and add some favorable lateral contacts. On the other hand, the formation of such lateral contacts between middle points in the chain induces a decrease in the configurational entropy with respect to a single ring. The balance between the changes in the configurational energy and entropy associated to the formation of multiloop structures depends on the system dimensionality: the presence of a steric or adsorbing surface imposes a two-dimensional arragement of the chains, leading to a significant decrease in their configurational degrees of freedom. Due to this entropy reduction mechanism, the formation of multiloop chains requires a smaller change of entropy in two-dimensional systems than in the bulk, thus it is favored in a broad range of parameters. Nevertheless, we expect that multiloop configurations will be observed in bulk for low enough temperatures, when energetic contributions overcome the entropic ones.

## IV. SUMMARY AND CONCLUDING REMARKS

We have studied the equilibrium behavior of a single flexible supramolecular magnetic filament in bulk as a function of the dipolar coupling parameter,  $\lambda$ , and the chain length.

The study has been carried out by means of Langevin molecular dynamics simulations using a bead-spring model of linked dipoles. Despite the fact that the dipoles in our model are free to rotate in any direction, they adopt a persistent head-to-tail alignment with the chain backbone for values of the dipolar coupling parameter above the limiting condition for stable self-assembly of MNPs,  $\lambda > 3$ .

Three different structural regimes and a chain closure transition have been found in our model: an open coil compaction regime for  $\lambda \leq 2$ , in which the dipoles are poorly aligned and form small aggregates of favorable lateral contacts; an open coil expansion regime for  $2 \leq \lambda \leq 6$ , in which the onset of the ferromagnetic alignment of the dipoles takes place; a magnetic flux closure transition at  $\lambda \sim 6$ , signaling the separation between the entropy and energy dominated structures; and finally, for  $\lambda \gtrsim 6$ , a regime of closed ring-like structures that tend to an ideal ring as  $\lambda$  increases.

We have analyzed the local stiffening of the chain induced by the increasing local alignment of the dipoles with  $\lambda$ , as well as the significant impact of the chain length on the equilibrium behavior of the system and its configurational entropy. We also discussed in our three-dimensional system the absence of multiloop structures like the ones found theoretically and experimentally in two-dimensional systems. We attributed this fact to the excess of configurational entropy in the bulk within the range of parameters explored.

Our results are found to be consistent with the known properties of self-assemblies of free MNPs. However, we have shown that the chain connectivity makes a difference with respect to dispersions and assemblies of free magnetic particles by imposing a more coherent and predictable behavior. This suggests that magnetic filaments can have advantages as building blocks for the synthesis of complex magnetic nanostructures.

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