

Relating the length of a magnetic filament with solvophobic, superparamagnetic colloids to its properties in applied magnetic fields

Deniz Mostarac

Computational and Soft Matter Physics, University of Vienna, 1090, Vienna, Austria

Ekaterina V. Novak

Department of Theoretical and Mathematical Physics, Ural Federal University, 620000, Ekaterinburg, Russia

Sofia S. Kantorovich 

*Computational and Soft Matter Physics, University of Vienna, 1090, Vienna, Austria
and Research Platform Mathematics-Magnetism-Materials, University of Vienna, 1090, Vienna, Austria*



(Received 28 April 2023; accepted 8 September 2023; published 1 November 2023)

The idea of creating polymer-like structures by crosslinking magnetic nanoparticles (MNPs) opened an alternative perspective on controlling the rheological properties of magnetoresponsive systems, because unlike suspensions of self-assembled MNPs, whose cluster sizes are sensitive to temperature, magnetic filaments (MFs) preserve their initial topology. Considering the length scales characteristic of single-domain nanoparticles used to create MFs, the MNPs can be both ferro- and superparamagnetic. Moreover, steric or electrostatic stabilization might not fully screen van der Waals interactions. In this paper, using coarse-grained molecular dynamics simulations, we investigate the influence of susceptibility of superparamagnetic MNPs—their number and central attraction forces between them—on the polymeric, structural, and magnetic properties of MFs with varied backbone rigidity. We find that, due to the general tendency of MFs with superparamagnetic monomers to bend, reinforced for colloids with a high susceptibility, properties of MFs vary greatly with chain length.

DOI: [10.1103/PhysRevE.108.054601](https://doi.org/10.1103/PhysRevE.108.054601)

I. INTRODUCTION

The idea of smart, magnetoresponsive materials has brought forth a variety of soft matter systems [1–6] since magnetic fluids were first synthesized [7]. Such materials, which are responsive to magnetic fields, can be made by combining magnetic micro- and nanoparticles (MNPs) with conventional soft materials, such as fluids or gels. Out of these systems, magnetic filaments (MFs) [8,9], first synthesized as micron-sized magnetic-filled paramagnetic latex beads forming chains [10,11], open up a plethora of potential applications [12–15]. They have been experimentally investigated as artificial swimmers [16], for cellular engineering uses [17,18], and as biomimetic cilia designs [19,20], just to name a few.

Even though synthesis techniques of MFs are now rather diverse and powerful [9,12,19,21–33], there is no clear recipe for how to create a polymer-like, supracolloidal chain that exhibits the desirable “polymeric” flexibility and a significant magnetoresponsiveness that supplants the magnetic response of the monomers—magnetic nanoparticles. Recent advances in DNA origami technology and programmable DNA-MNP assembly techniques have shown a potential to produce flexible, nanoscale MFs, with a highly controllable microstructure [34–41]. As it stands, such filaments have not been achieved.

Theoretically, MFs have mostly been explored in bulk [42–49]. Their behavior when exposed to an external magnetic field has also been scrutinized [50–56]. Theoretical work has been done on filaments in the context of artificial swimmers [57–59], biomedical applications [60–62], micromixers [63], as well as designs for cargo capture and transport [64]. Magnetic filaments or fibers on the micron scale are in general valuable for tuning the effective viscosity of magnetorheological suspensions [65]. Magnetic and structural properties of MFs have been studied from the point of view of the magnetic nature of colloids they consist of, and from a crosslinking approach [66]. Furthermore, properties of MFs with superparamagnetic monomers exhibiting central attraction forces have been investigated [67].

Key insights from previous works that depict the relevance of this work can be summarized in the following:

(1) The crosslinking approach is of major importance for MFs, strongly affecting both their magnetic and structural properties.

(2) MFs with superparamagnetic colloids can not only exhibit a more substantial magnetic response to applied magnetic fields than their counterparts with ferromagnetic ones, but also exhibit qualitatively different behavior that is dependant on monomer number.

(3) Magnetic colloids are never completely impartial towards the solvent they are in, and synthesis attempts have underlined van der Waals (vdW) forces as an uncircumventable element of a prospective experimental

*sofia.kantorovich@univie.ac.at

system, the effect of which scales with monomer number and affects the magnetic and structural properties of MFs tremendously.

Permanent, flexible, linear conformations of magnetizable colloids are a key component of future technologies that leverage magnetoresponsiveness. Therefore, it is important to understand the relation between filament length and its properties, especially if they consist of superparamagnetic colloids exhibiting central attraction. To the best of our knowledge, there are currently no comparative studies that scrutinize the properties of a single nanoscopic MF as a function of monomer number, where the colloids can interact via a central attraction and that take into account the nonlinear contributions to the magnetization of superparamagnetic monomers, while exposed to an external magnetic field. In this manuscript, we employ molecular dynamics (MD) simulations to fill the gap in understanding of fundamental properties of magnetic filaments. We discern two crosslinking approaches which allow us to contextualize the effects of dipole interactions, magnetization, and central forces in terms of either a rather flexible filament backbone or a backbone that has significant stiffening against bending. Even though we do not directly address the mechanical properties of MFs here, as we previously did in Refs. [68,69] for the case of no central attraction between monomers, or as it has been done in Refs. [14,48,70,71], we can get a qualitative picture of the elasticity by looking at gyration radii [72]. We present a comparative analysis of MF equilibrium, structural, and magnetic properties in constant, homogeneous magnetic fields. With this, we envelop the phenomenology of a single magnetic filament with superparamagnetic monomers and link it to broadly applicable and generalizable trends and guidelines for prospective experimental systems. Specifically, the content of this work should prove useful for low-density suspensions of polymer-like structures containing nanoscopic magnetic colloids in a poor solvent, and give a baseline estimate for how chain length distribution in such a suspension affects its properties at equilibrium.

The paper is structured as follows: in Sec. II we outline our coarse-grained modeling approach. This includes the simulation protocol, magnetic and vdW interactions, a discussion on the magnetic properties of MNPs, and modeling of superparamagnetic MNPs, as well as a detailed account of units. We proceed to discuss our results in Sec. III. We present how the crosslinking approach and the interplay between central attraction and the dipole interactions affect the structural and magnetic properties of filaments with magnetizable, superparamagnetic colloids. In Sec. IV, we provide a summary and prospects of our study.

II. METHODOLOGY

A. Simulation method

Using the ESPResSo software package [73], we perform molecular dynamics simulations for different monomer numbers N , saturation magnetization $\mu_{\max}$, and dimensionless applied field strength $H \equiv |\vec{H}|$, where $\vec{H}$ is always directed along the z axis. The carrier fluid was represented implicitly via the Langevin thermostat at fixed temperature T [74]. In

practice it means that the Langevin equations of motion are integrated over time t numerically:

$$M_i \frac{d\vec{v}_i}{dt} = \vec{F}_i - \Gamma_{Tl} \vec{v}_i + 2\vec{\xi}_i^{Tl}, \quad (1)$$

$$I_i \frac{d\vec{\omega}_i}{dt} = \vec{\tau}_i - \Gamma_R \vec{\omega}_i + 2\vec{\xi}_i^R, \quad (2)$$

where for the i th particle in Eq. (1), M_i is, in general, a rank-two mass tensor that in our case of isotropic monomers reduces to a scalar, $\vec{F}_i$ is the force acting on the particle, and $\vec{v}_i$ denotes the translational velocity. Γ_{Tl} denotes the translational friction tensor that once again in our particular case reduces to one scalar friction coefficient. Finally, $\vec{\xi}_i^{Tl}$ is a stochastic force, modeling the thermal fluctuations of the implicit solvent. Similarly, in Eq. (2), I_i denotes the i th particle inertia tensor (scalar for a homogeneous sphere), $\vec{\tau}_i$ is torque acting on it, and $\vec{\omega}_i$ is particle rotational velocity. As for the translation, Γ_R denotes the rotational friction tensor that reduces to a scalar for our monomers, and the $\vec{\xi}_i^R$ is a stochastic torque serving for the same purpose as $\vec{\xi}_i^{Tl}$. Both stochastic terms satisfy the conditions on their time averages [75]:

$$\begin{aligned} \langle \vec{\xi}^{R/Tl} \rangle_t &= 0, \\ \langle \vec{\xi}_l^{Tl/R}(t) \vec{\xi}_k^{Tl/R}(t') \rangle &= 2\Gamma_{Tl/R} k_B T \delta_{l,k} \delta(t - t'), \end{aligned} \quad (3)$$

where $k, l = x, y, z$.

Forces and torques in Eqs. (1) and (2) are calculated from interparticle interaction potentials. In all our simulations here, we used no periodic boundary conditions, as the focus is always on a single polymer-like chain per simulation box. For the integration, the velocity Verlet algorithm was used [76] with a time step of 0.01 (see Sec. II C for more detail on the simulation units and their relation to experimental values). The long-range dipole-dipole pair interactions are simulated using direct summation. Initial filament backbone orientations are uniformly distributed on the surface of a sphere. After making sure that the system relaxes into an equilibrium, field-free configuration by running an integration cycle for 10^8 integration steps, we switch on the external magnetic field and start measuring. To obtain statistically significant results, we always present averages over 40 independent simulation runs, and make sure that the snapshots we use for “measuring” are sufficiently far apart from each other to minimize correlations, by performing 3×10^7 integrations, sampling at intervals separated by 10 000 integrations each.

B. Modeling details

We model MFs formed by monodisperse, spherical, superparamagnetic monomers, with a characteristic diameter σ using a well-established and proven bead-spring representation of a polymer. The central attraction between the monomers is given by the Lennard-Jones potential:

$$U_{LJ}(r) = 4\varepsilon_{\text{vdW}} \{ (\sigma/r)^{12} - (\sigma/r)^6 \} \quad (4)$$

where ε_{vdW} is the depth of the potential that determined the energy scale of the attraction or repulsion. It is implied that the nature of physical or chemical processes that lead to vdW

forces, and distinctions between them, are unimportant, as long as their action is well captured by uniform central attraction. This is why throughout this work, we use solvophobicity and vdW forces interchangeably, as at equilibrium they cannot be distinguished in any substantial way from effective, central attraction forces between the colloids. Since we are exploring single filament properties at equilibrium, the Langevin dynamics coupled together with an effective central attraction implicit representation of a solvent is sufficient and accurate.

The long-range magnetic interparticle interactions are accounted for by the standard dipole-dipole pair potential:

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

where the interparticle distance is $r = |\vec{r}_{ij}|$, and $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ is the displacement vector connecting the centers of monomers i and j with dipole moments $\vec{\mu}_i$ and $\vec{\mu}_j$, respectively. Furthermore, we consider Zeeman interactions coming from the presence of an external magnetic field $\vec{H}$:

$$U_H(\vec{H}, \vec{\mu}_i) = - \sum_{i=0}^N \vec{H} \cdot \vec{\mu}_i. \quad (6)$$

Phenomenology of superparamagnetic MNPs is simulated using the model introduced in Mostarac *et al.* [66], where the MNPs are considered as perfectly isotropic, magnetizable colloids, which are also susceptible to dipole fields $\vec{H}_d$ in addition to the external magnetic field applied, $\vec{H}$. The total magnetic field $\vec{H}_{\text{tot}}$ is the sum $\vec{H}$ and $\vec{H}_d$. The latter field, created by particle j , at position $\vec{r}_0$ is given by

$$\vec{H}_d = \frac{3\vec{r}_{0j} \cdot \vec{\mu}_j}{r_{0j}^5} \vec{r}_{0j} - \frac{\vec{\mu}_j}{r_{0j}^3}. \quad (7)$$

We define the dipole moment $\vec{\mu}_i^s$ of an i th superparamagnetic particle at a given temperature T as

$$\vec{\mu}_i^s = \mu_{\text{max}} L\left(\frac{\mu_{\text{max}} |\vec{H}_{\text{tot}}|}{k_B T}\right) \frac{\vec{H}_{\text{tot}}}{H_{\text{tot}}}, \quad (8)$$

where $\mu_{\text{max}} = |\vec{\mu}_{\text{max}}|$ denotes the modulus of the maximal magnetic moment of the particle, $\vec{\mu}_{\text{max}}$. Here, k_B is the Boltzmann constant and $L(\alpha)$ is the Langevin function:

$$L(\alpha) = \coth(\alpha) - \frac{1}{\alpha}. \quad (9)$$

Essentially, we use a classical magnetization law for a non-interacting system of superparamagnetic colloids and extend it so that the interactions are accounted for as a nonlinear contribution to the magnetization.

Regarding the modeling of monomer crosslinking, we discern two approaches. On one side, we realize filaments with a flexible backbone via finitely extendable spring potential U_{FENE} bonds, attached to monomer centers. This crosslinking restricts only on the translational degrees of freedom between the monomers, and we refer to it as plain crosslinking. When defined as a function of the center-to-center distance r , U_{FENE} potential takes the form

$$U_{\text{FENE}}(r) = \frac{-K_f r_f^2}{2} \ln \left\{ 1 - \left(\frac{r}{r_f} \right)^2 \right\}, \quad (10)$$

where r_f and K_f are the maximum extension and the rigidity bond, respectively. We ensure close contact, without introducing any energetic penalty on rotation of the monomers. Therefore, the head-to-tail arrangement of the dipole moments is achieved purely through the cooperative influence of the magnetic dipolar field generated by neighboring monomers and the external magnetic field (if applied). Alternatively, we scrutinize the effects of additional interparticle correlations and backbone rigidity by contrasting a purely U_{FENE} backbone to one with added isotropic bending pair potential U_{bend} for each consequent three-particle set, given by

$$U_{\text{bend}}(\phi) = \frac{K_b}{2} (\phi - \phi_0)^2, \quad (11)$$

where ϕ is the angle between the vectors spanning from particle i to its nearest-neighbor particle pair $(i-1, i+1)$, $i \in [2, N-1]$. K_b is the bending constant, while $\phi_0 = \pi$ is the equilibrium bond angle. The expression in Eq. (11) is a harmonic, angle-dependent potential. Through this work, we refer to the above-described crosslinking model as constrained crosslinking.

C. Reduced units and mapping to physical parameters

In this subsection we give a detailed overview of the units used in our simulations. We communicate to what SI scale the units in our simulations (reduced units) correspond—in other words, we provide a mapping of reduced units to SI units.

The time scale in a simulation is $[t] = 2.14 \times 10^{-8}$ s. We set the reduced temperature of the Langevin thermostat to be $k_B T = 1$, corresponding to 298.15 K. The energy in our simulations is measured in units of $k_B T$. We consider two values of the reduced saturated magnetic moment $\mu_{\text{max}}^2 = |\vec{\mu}_{\text{max}}|^2 = 1$ and $\mu_{\text{max}}^2 = 3$, for a range of reduced external magnetic fields $H \leq 6$. Given a choice of a particular magnetic nanoparticle, such as using magnetite nanoparticles coated with a thin layer of stabilizing agent (i.e., oleic acid coating, 1.5 nm thick), in the case of $\mu_{\text{max}}^2 = 1$, σ corresponds (not uniquely) to a colloid with a magnetic core of 11 nm with a dipole moment of 3.35×10^{-19} Am², whereas for $\mu_{\text{max}}^2 = 3$, σ corresponds (not uniquely) to a colloid with a magnetic core of 15 nm with a dipole moment of 8.5×10^{-19} Am². The length scale is set equal to the monomer diameter. The maximum of the applied magnetic field range we explored represents moderate fields of only 0.072 T, for MNPs with $\mu_{\text{max}}^2 = 1$ and 0.05 T, for MNPs with $\mu_{\text{max}}^2 = 3$. We chose magnetite as a reference as it is one of the most commonly used magnetic materials in magnetic soft matter. The chosen range of magnetic field strength spans from an initially weak magnetic response to the saturation magnetization of MNPs. The factor K_f of the potential given in Eq. (10) is set to $K_f = 10$. The maximum extension of the FENE bond r_f , is set to $r_f = 2\sigma$. The bending constant K_b of the harmonic angle-dependent potential given in Eq. (11) is set to $K_b = 3.2$.

Values of N we explore in this work are sensible relative to the theoretical model introduced in Mostarac *et al.* [66] to rationalize tendencies of magnetic filaments with superparamagnetic monomers to bend. By combining the Flory approach and direct calculations of dipolar interactions in a folded filament, we understood that, as a function of monomer number,

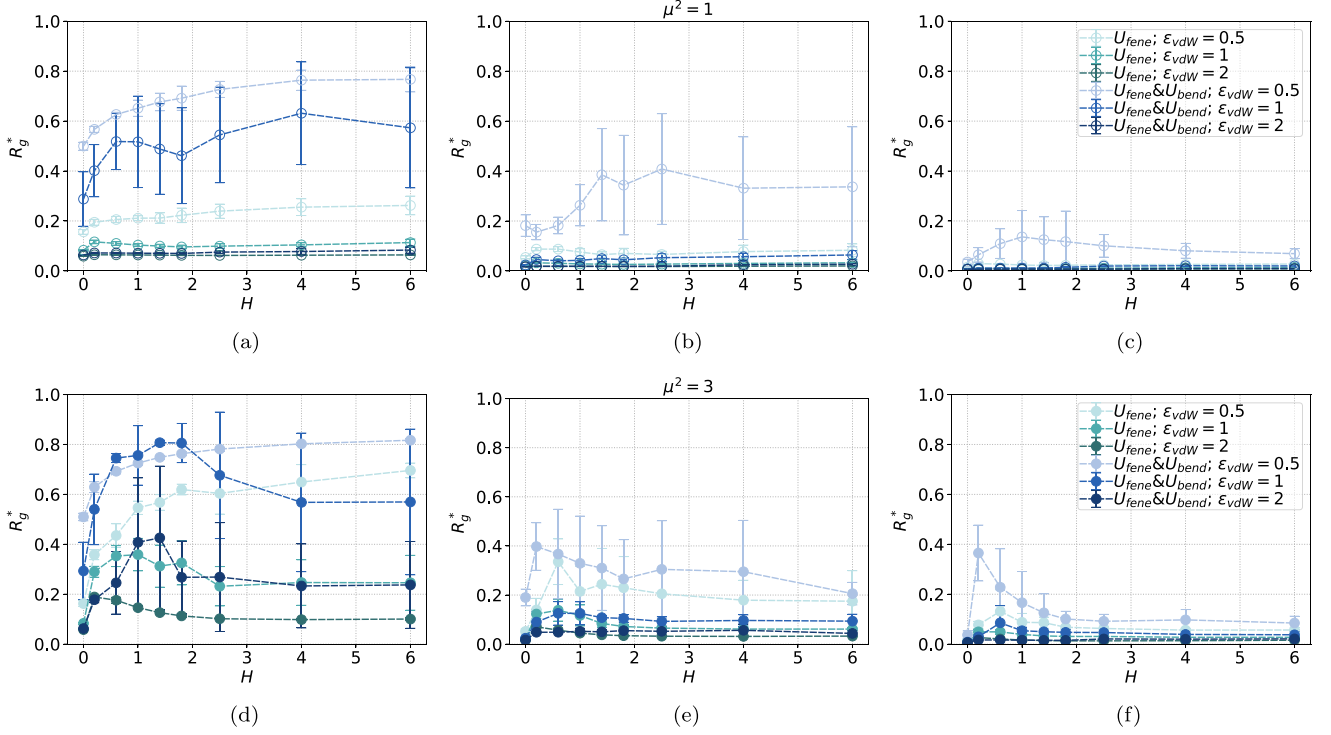


FIG. 1. Normalized radius of gyration (R_g^*), plotted as a function of H . Each subplot is showing profiles corresponding to MFs with colloids exhibiting various strengths of central attraction ϵ_{vdW} and crosslinking. Subplots in the same row contain results with the same colloid saturation magnetization, where in [(a)–(c)], $\mu_{\text{max}}^2 = 1$ (hollow symbols); in [(d)–(f)], $\mu_{\text{max}}^2 = 3$ (filled symbols). Subplots in the same column contain results for MFs with the same number of monomers, where in (a) and (d), $N = 20$; (b) and (e) are showing $N = 50$; (c) and (f) are showing $N = 100$. Color coding for different ϵ_{vdW} and crosslinking is explained in the legends. Error bars are calculated as the standard deviation of R_g^* across 40 independent simulations.

it can be advantageous for a filament with superparamagnetic monomers to bend both from the point of view of overall free energy and magnetic interactions. Therefore, we choose three values of N around a threshold length where this conclusion holds. We expect to see stark qualitative differences between filaments with $N = 20$ and $N = 50$. For $N = 100$, we expect results to be more similar to $N = 50$ than to $N = 20$.

III. RESULTS AND DISCUSSION

A. Conformations

To avoid irreversible aggregation due to attractive forces, one would try to render the background medium in a suspension as chemically transparent as possible and stabilize the magnetic colloids. Regardless, it remains a matter of fact that vdW forces will be present to some degree in real suspensions of MFs. Here, we focus on a magnetic filament that has a slight affinity towards its own species rather than the solvent. In this case, filaments form compact clusters [77] like those seen in Stockmayer systems [78–82], instead of open networks that would form in filament suspension without any central attraction present [83]. Earlier works on Stockmayer systems have considered ferromagnetic colloids. In this work, we study how the presence of vdW forces affects the properties of MFs with superparamagnetic monomers, as a function of monomer number. Such filaments have a tendency to bend into what we broadly call U-shaped conformations, resulting in a remarkably diverse and rich conformational

spectrum, a phenomenology that is bound to be affected by vdW forces. A standard way to analyze the polymeric properties of a polymer-like structure is to calculate the gyration radius $R_g = \sqrt{\lambda_1^2 + \lambda_2^2 + \lambda_3^2}$, where $\lambda_1 > \lambda_2 > \lambda_3$ are the eigenvalues of the gyration tensor:

$$G_{\mu\nu} = \frac{1}{N} \sum_{i=1}^N (r_{i,\mu} - r_{\text{cm},\mu})(r_{i,\nu} - r_{\text{cm},\nu}) \quad (12)$$

where $r_{i,\mu}$ and $r_{\text{cm},\mu}$ are the μ th Cartesian components of the position of the i th monomer and the center of mass, respectively. The summation is carried over all N monomers in a filament. Experimentally, R_g is one of the typical measurements for polymers as, for example, in Ref. [72]. In the case of larger supramolecular polymer-like structures, the gyration radii can be extracted from atomic force microscopy and transmission electron microscopy data, as, for example, in Ref. [40]. Here, we use R_g^* to denote R_g normalized by its value for a rod with a length corresponding to an equivalent number of monomers at touching distance.

Figures 1(a)–1(c) show that filaments with plain crosslinking (green), composed of weakly magnetic monomers ($\mu_{\text{max}}^2 = 1$), exhibit largely flat R_g^* profiles that vary by at most 10% with monomer number. Even the shortest MFs we explored essentially coil up and remain so across the range of H explored. In this case magnetic interactions are weak and are dominated by entropy. However, if MFs contain strongly magnetic monomers ($\mu_{\text{max}}^2 = 3$), shown in Figs. 1(d)–1(f),

dipole-dipole interactions can compete with entropy. In the weak central attraction region ($\varepsilon_{\text{vdW}} = 0.5$), for $N = 20$, R_g^* suggests that MFs unravel into conformations characteristic of a head-to-tail dipole arrangement, even for weak applied fields ($H < 1$). With increasing N , we see the joined action of entropy, vdW forces, and bent-backbone conformations becoming more favorable and persistent. The differences in R_g^* decrease as monomer number increases due to the coiling. Central attraction between the monomers leads to more compact conformations of MFs, as the system tries to minimize the contact surface with the solvent. Filaments with superparamagnetic monomers can bend in an applied magnetic field to obtain a significant gain in entropy, and depending on filament length, can in principle do so without a loss in magnetic energy [66], meaning that we attribute the overall shape of R_g^* profiles to the local orientation of dipole moments. Consequently, we see instances where R_g^* decreases with increasing H strength. Furthermore, bent-backbone filament conformations collapse due to central attraction. For $\varepsilon_{\text{vdW}} \geq 1$, central attraction is strong enough to compete with dipole-dipole interactions. Therefore, for plain crosslinking, the differences between the R_g^* profiles, regardless of μ_{max}^2 , are small and mostly constrained to the low field region, where the bending tendencies of MFs with superparamagnetic monomers are less pronounced. For $H \geq 2$, R_g^* profiles are indistinguishable for a given N .

Increase in intermonomer correlations exacerbates the variance in R_g^* , as can be seen for constrained crosslinking in Fig. 1 (blue). Constrained crosslinking leads to a backbone that is overall stiffer and resists bending. On one side, the head-to-tail dipole arrangement and resistance to bending induced by the constrained crosslinking favor elongation of the backbone along $\vec{H}$. On the other side bent-backbone conformations are favorable from the point of view of entropy, vdW interactions, and can even be magnetically favorable. Filaments with constrained crosslinking follow broadly similar trends, while being on average more elongated than their counterparts with plain crosslinking. The fact that coiling is also favorable from the point of view of magnetic interactions is visually accessible. While not a feature specific to constrained crosslinking, the added rigidity against bending acting against entropy and central attraction, leading to higher R_g^* values, highlights instances where increase in H flips the balance of forces in favor of more coiling. It is interesting to note the particularly wide error bars for constrained crosslinking in Fig. 1(d) for $\varepsilon_{\text{vdW}} \geq 1$ or in Fig. 1(e) for $\varepsilon_{\text{vdW}} = 0.5$. This is an energetically contentious region for MFs. For $N \geq 50$ there are bent-backbone conformations that are magnetically favorable, while for $N = 20$ they correspond to local energy minima. In both cases, MFs spend considerable time in such conformations and, therefore, exhibit a lot of variance in R_g^* . Central attraction favors bent-backbone and collapsed conformations, hence increasing ε_{vdW} and/or N decreases the variance of R_g^* . Regardless, we note mostly coiled filament conformations, except for short $N = 20$ MFs. Higher monomer number favors collapsed conformations. Differences in R_g^* based on μ_{max}^2 , for a given N , are small and mostly constrained to the low field region. For constrained crosslinking, this is true even for weaker central attraction, $\varepsilon_{\text{vdW}} \leq 0.5$. Additional intermonomer correlations,

introduced by constrained crosslinking, support the favorable head-to-tail dipole arrangement. Therefore, R_g^* profiles between MFs with weakly and strongly magnetic monomers are more similar for constrained than for plain crosslinking.

B. Neighbor analysis

Considering what we learned from Fig. 1, it is interesting to scrutinize the local structure within the compact conformations MFs form. Specifically, we want to understand whether these compact structures keep an ordered internal structure and a favorable dipole moment configuration as well. To do so, we investigate the number of nearest neighbors as a function of ε_{vdW} and H , and the number of magnetically favorable neighboring monomers in a filament for different crosslinking, μ_{max}^2 and N , both of which are shown in Fig. 2. Neighbors of a monomer i are all monomers $j \neq i$ whose center is within the volume of a sphere of radius 1.3σ centered at the monomer i . Among the neighboring monomers, we can additionally count only the ones whose dipole moment is favorably orientated with respect to the dipole moment of the i th monomer ($U_{dd} < 0$).

When no external magnetic field is applied, MFs form highly compact structures, where each monomer can have up to seven nearest neighbors; this value is a growing function of ε_{vdW} . Once a magnetic field is applied, the effect of dipolar interactions is depicted in the contrast of the number of total neighbors for subplots with different μ_{max}^2 . We can see that for monomers with a low magnetic susceptibility, the onset of magnetic interactions affects the total number of magnetic neighbors only slightly, with marginal increase as a function of H . Strong central attraction forces and entropic coiling offset the energetic penalty of weakly magnetic monomers in unfavorable configurations. This is also reflected in the overall low number of magnetically favorable neighbors, unless a strong external magnetic field is applied. In this case, since at saturation magnetization the weakly magnetic monomers in our simulations exhibit dipole-dipole interactions comparable to thermal fluctuations, and in a strong applied field are coaligned with it with very little variance, they manage to achieve very compact structures that still have an overall magnetically favorable internal structure. It is therefore also due to dipole interactions that MFs with highly susceptible monomers exhibit a pronounced increase in the number of total neighbors with growing magnetic field. For strongly magnetic colloids, unless central attraction forces dominate, dipole-dipole interactions act against the structural collapse of the backbone and the overall number of magnetically favorable neighbors is high. However, as Zeeman coupling increases, backbone bending becomes advantageous in terms of both overall free energy and magnetic interactions, so we see a pronounced increase in total number of neighbors without detrimentally affecting the number of magnetically favorable ones.

Regardless of μ_{max}^2 , the orientational correlations induced by constrained crosslinking increase the fraction of magnetically favorable neighbors compared to plain crosslinking in the low applied field region, while in the high field region they decrease it slightly. This underlines the importance of the interplay between dipolar interactions crosslinking

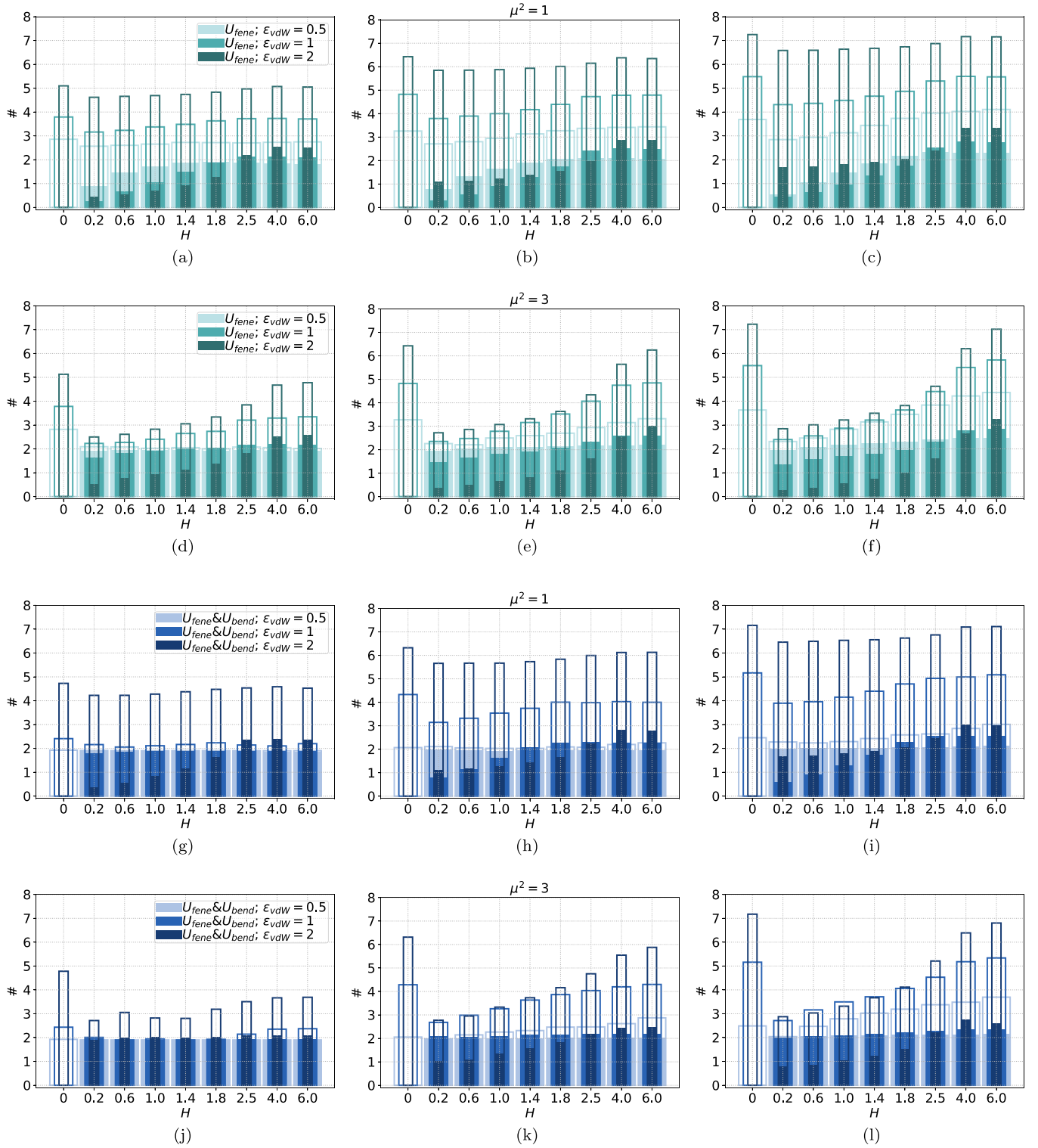


FIG. 2. Number of neighbors each monomer in a filament has versus magnetic field strength H . The hollow part of each bar shows the total number of neighbors while the filled part shows the part of neighbors that are magnetically favorable. Each subplot shows MFs with colloids exhibiting various strengths of central attraction ϵ_{vdW} . Subplots in the same row contain results for MF with the same colloid saturation magnetization, where [(a)–(i)] correspond to $\mu_{\max}^2 = 1$, while [(d)–(l)] correspond to $\mu_{\max}^2 = 3$. Subplots in the same column contain results for MFs with the same number of monomers, where in (a), (d), (g), and (j), $N = 20$; (b), (e), (h), and (k) show $N = 50$; and (c), (f), (i), and (l) show $N = 100$. Color coding for different ϵ_{vdW} and crosslinking is explained in the legends. Bars are shown with varying thickness to improve legibility, where thickness decreases with increasing ϵ_{vdW} .

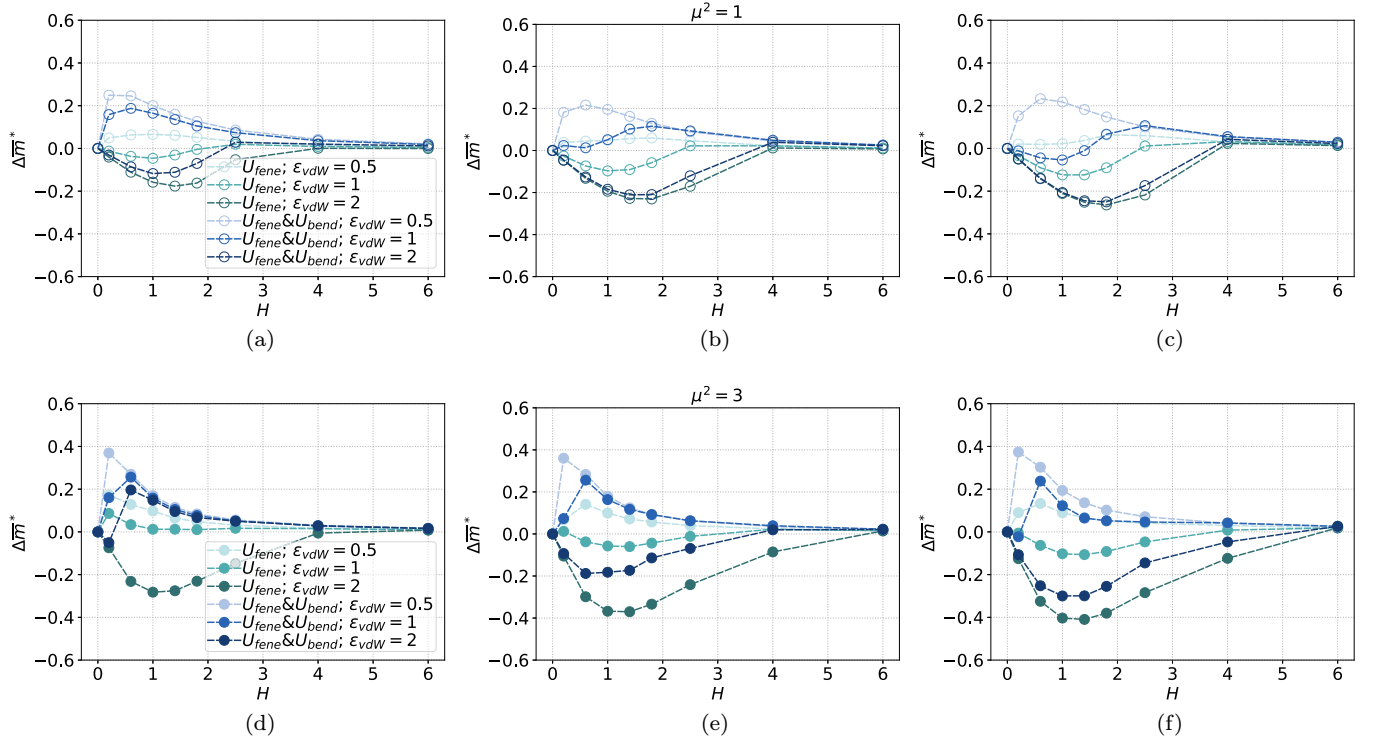


FIG. 3. The difference between the normalized filament magnetization and magnetization of a semiconcentrated ferrofluid, predicted by MMFT [Eq. (13)], denoted with $\Delta\bar{m}^*$, as a function of the dimensionless magnetic field strength H . Each subplot is showing $\Delta\bar{m}^*$ profiles corresponding to MFs with colloids exhibiting various strengths of central attraction ε_{vdW} and crosslinking. Subplots in the same row contain results with the same colloid saturation magnetization, where in [(a)–(c)], $\mu_{\text{max}}^2 = 1$ (hollow symbols); in [(d)–(f)], $\mu_{\text{max}}^2 = 3$ (filled symbols). Subplots in the same column contain results for MFs with the same number of monomers, where in (a) and (d), $N = 20$; (b) and (e) show $N = 50$; (c) and (f) show $N = 100$. Color coding for different ε_{vdW} and crosslinking is explained in the legends. Error bars are comparable to symbol size and are as such not shown.

induced orientational correlations. Where magnetic interactions are weak, added interparticle correlations stemming from the crosslinking help enforce a favorable head-to-tail dipole arrangement, while if the magnetic interactions are strong enough, it restricts how dipoles can rearrange to relax the magnetostatic energy. The effect of entropy is reflected in the increase of overall number of neighbors with increasing N . The impact of monomer number is only quantitative. We can see an overall increase in monomer neighbors with increasing N is slightly less pronounced in MFs with plain crosslinking than in their counterparts with constrained crosslinking, mainly because of the greater backbone flexibility inherent to plain crosslinking. We see that, as expected, the results for $N = 50$ are more similar to the results for $N = 100$ than $N = 20$. For such chain lengths, backbone bending is advantageous in terms of both overall free energy and magnetic interactions. For shorter $N = 20$ filaments, elongated conformations are still slightly more advantageous in terms of magnetic interactions.

Finally, it is worth noting that, as seen in Fig. 1, MFs form highly coiled structures, far remote from an elongated or rod-like conformation that would be typical for MFs with ferromagnetic colloids in a good solvent. However, these are not necessarily collapsed, aggregate-like structures, as understood from the relatively low total number of neighbors for MFs with strongly magnetic colloids in a weak applied field. In conjunction, this means that MFs assume conformations

resembling structures that appear to a classical Stockmayer fluid, where magnetic colloids arrange in chains, head to tail, forming a globally circular pattern. These are noncollapsed weaving loops of dipoles following the dipole field flux. As the applied field strength increases, given the magnetizable nature of superparamagnetic colloids, the dipole moments orientation becomes coaligned with the external magnetic field, at which point collapsed filament conformations become favorable from the point of view of magnetic interactions. This finally leads to the structural collapse of the backbone. However, in contrast to clusters of ferromagnetic colloids generally and polymer-like structures containing them, MFs with superparamagnetic monomers maintain an amicable magnetic response to applied magnetic fields.

C. Magnetic response

In this section we analyze the magnetization of MFs and its relation to the number of monomers and their susceptibility.

Looking at Fig. 3, we can see how the structural collapse of the filament backbone, facilitated by central attraction, affects the magnetic response of MFs, quantified by the difference between the normalized filament magnetization and the magnetization of a semidilute ferrofluid, denoted with $\Delta\bar{m}^*$, as a function of the dimensionless magnetic field strength H . The normalized magnetization $\bar{m}^*$ is the total magnetic moment of a filament, normalized by the number of monomers

and $\mu_{\max}$, as a function of H . The magnetic response of a semidilute ferrofluid is well described by the second-order modified mean-field theory (MMFT2) [84]:

$$\begin{aligned} \mu &= \rho^* \mu_{\max} L(\mu_{\max} H_e), \\ H_e &= H + \frac{1}{3} \mu_{\max} \rho^* L(\mu_{\max} H) \\ &\quad + \frac{1}{48} (\mu_{\max} \rho^*)^2 L(\mu_{\max} H) \frac{dL(\mu_{\max} H)}{dH}, \end{aligned} \quad (13)$$

where ρ^* is the magnetic particle number density. Here, we assume that for a given value of H , all MNPs are constrained to a volume $V = 4\pi R_g^3/3$, so $\rho^* = N/V$. Generally, MFs are more responsive to external magnetic fields than a ferrofluid, and in the absence of central attraction forces, $\bar{m}^*$ is independent of monomer number. However, vdW forces scale with filament length, and affect and restrict the conformational phase space MFs can explore, making it interesting to consider $\bar{m}^*$ in that context also. Central attraction tends to push dipole moments in rather frustrating arrangements. We see that as ε_{vdW} increases, MFs become significantly less responsive to low- or moderate-strength external magnetic fields, compared to a semidilute, nonclustering ferrofluid. We see up to 20% lower $\Delta\bar{m}^*$ for strongly magnetic colloids, and up to 40% lower $\Delta\bar{m}^*$ for weakly magnetic ones. This underlines why it is crucial to avoid agglomeration of systems containing magnetic colloids. The magnetic response of MFs with plain crosslinking decreases tremendously with increasing central attraction strength. MFs with weakly magnetic monomers exhibit a magnetic response similar to the predictions of MMFT2 only for relatively strong magnetic fields or low central attraction strength. It can be seen in Figs. 3(d)–3(f), showing $\Delta\bar{m}^*$ for MFs with strongly magnetic monomers, that having strongly magnetic monomers alleviates the issue somewhat. Regardless, the loss in magnetic response is greater for longer filaments, where between $N = 20$ and $N = 100$ we see up to 10% lower magnetization, depending on ε_{vdW} and H strength. It should be clear by this point that plain crosslinking severely limits the magnetic response of MFs, particularly when vdW forces are present, where one can expect a system with a magnetic response to a semidilute ferrofluid at best. However, MFs with constrained crosslinking fare much better. In fact, if vdW forces are not too strong ($\varepsilon_{\text{vdW}} \leq 1$), $\Delta\bar{m}^*$ profiles corresponding to MFs with constrained crosslinking are representative of systems that are more magnetoresponsive than conventional magnetic fluids. Even for $N = 100$ filaments, we see up to 20% improvement for MFs with weakly magnetic monomers and up to 40% improvement for strongly magnetic ones in magnetoresponsiveness compared to MMFT2 predictions. The additional intermonomer correlations and resistance against bending complement and favor the head-to-tail dipole moment configuration. In effect, for strongly magnetic $\mu_{\max}^2 = 3$ monomers, constrained crosslinking suffices to almost completely offset the reduction in magnetoresponsiveness of shorter MFs ($N = 20$) due to vdW forces, while for long chains $N = 100$ this is the case if $\varepsilon_{\text{vdW}} \leq 1$. In order to visualize some of the key points from the discussion above, in Fig. 4, we include snapshots of characteristic equilibrium conformations for MFs with $N = 50$ monomers, plain or constrained crosslinking, in a weak

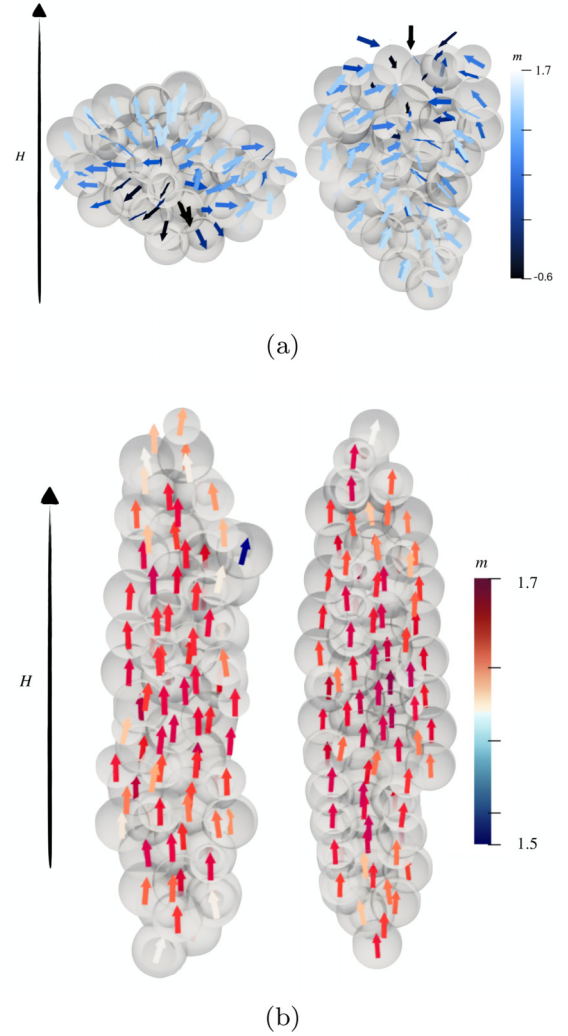


FIG. 4. Simulation visualization of $N = 50$ MFs with plain (left) and constrained crosslinking (right), with highly magnetic monomers ($\mu_{\max}^2 = 3$), in a weak magnetic field ($H = 1$) (a), and in a strong magnetic field ($H = 6$) (b), where monomers have a strong affinity toward agglomeration ($\varepsilon_{\text{vdW}} = 2$). Color bar denotes the span of monomer magnetization for the configurations shown.

[Fig. 4(a)] or strong [Fig. 4(b)] external magnetic field. Each subfigure consists of two snapshots. The left snapshot in a subfigure is a snapshot of a filament with plain crosslinking, whereas the right one depicts a filament with a constrained crosslinking. The direction of the field is denoted by a black arrow on the left. The color bar on the right, common for both snapshots in a subfigure, encodes the alignment with the external magnetic field of any particular dipole moment (magnetization). When a weak magnetic field is applied, the clusters are very compact. The dipole moments of individual monomers are not particularly aligned with the external magnetic field. This suggests that the dipole fields are the dominant factor that determines the structure of the cluster, whereas the external magnetic field mainly serves the purpose of inducing the dipole moments. The structure on the right in Fig. 4(a) is more extended because of the bending rigidity

brought by a constrained crosslinking. The difference between crosslinking becomes less important if a strong magnetic field is applied, as both conformations elongate along the external magnetic field direction as seen in Fig. 4(b). While the structure might be locally more frustrated, additional intermonomer correlations enforce an overall more organized structure where the configuration is dictated by the external magnetic field, as can be seen in Fig. 4(b). Here, one can also notice a mild increase in the magnetization if the crosslinking is constrained (right snapshot).

IV. CONCLUSIONS

This study posits that it is manifestly not feasible to completely screen central attraction forces between magnetic colloids. As such, given the nature of vdW forces, even the slightest affinity a colloid might have towards their own species rather than the solvent will greatly affect the properties of prospective polymer-like structures that contain magnetic colloids. Using coarse-grained molecular dynamics simulations, we investigated polymeric, structural, and magnetic properties of nanoscopic MFs with superparamagnetic monomers, in the presence of an effective central attraction between the monomers. In particular, we elucidate the implications of filament length, in conjunction with the crosslinking approach, monomer susceptibility, and central attraction strength.

We find that in an external magnetic field, MFs with a flexible backbone, where the rotational degrees of freedom between the monomers are decoupled, and the magnetic susceptibility of monomers is low assume very compact, collapsed conformations, regardless of the field strength. Alternatively, for more susceptible magnetic colloids, whether the backbone of a filament collapses and how compact the resulting structure is depends on the external magnetic field strength. With a strong central attraction, it is possible to observe a monomer packing close to the one characteristic of a body centered cubic lattice—seven or eight nearest neighbors surround each monomer, out of which, however, only two or three are favorable in terms of the dipole-dipole interaction energy. Although the validity of the previous statement depends on the number of monomers in a filament, having in mind the typical number of monomers in polymeric systems, the longest filaments we explored in this work are still relatively short. Therefore, our results suggest that, with vdW forces present, one should expect to encounter

compact in-field structures, which can resemble highly ordered structures—even if the energy scale of central attraction is lower than thermal fluctuations, we obtain structures that reach compactness that can rival, for example, the diamond cubic lattice, a well-ordered structure. This underlines the importance of the nonlinear contributions, that is, the contribution of dipole fields to the magnetization of superparamagnetic colloids, a key element without which such structures would simply not be possible. In collapsed, compact conformations, the colloids are forced into magnetically unfavorable alignments, which hinders the magnetoresponsiveness of MFs. The decrease in magnetization is more pronounced for more magnetically susceptible monomers: one might need to double the field strength to achieve magnetization of MFs with no vdW forces present.

For a backbone with rigidity against bending, however, the additional correlations, induced by the crosslinking, notably enhance the magnetoresponsiveness of MF in weak applied fields, particularly for highly susceptible monomers. Although we observe somewhat less compact conformations, the discussion from the paragraph above still applies. This underlines that one should consider that MFs with superparamagnetic colloids can fold with an external magnetic field applied. In this case, magnetically and entropically favorable bent-backbone conformations complement vdW interactions and lead to surprisingly compact collapsed in-field structures. Concomitantly, the degree to which colloids manage to form a head-to-tail dipole arrangement in conjunction with the intermonomer correlations stemming from the crosslinkers determines the magnetoresponsiveness of the overall structure, underlining the fact that crosslinking is the critical factor when engineering polymer-like systems that exhibit a significant responsiveness to external magnetic fields.

Currently, we are investigating suspensions of MFs with superparamagnetic monomers at equilibrium, and their dynamic response to external magnetic fields in an explicit solvent representation to homogeneous and time-dependant magnetic fields.

ACKNOWLEDGMENTS

This research has been supported by the Project SAM P 33748. E.N. was supported by Russian Science Foundation Grant No. 19-72-10033. Computer simulations were performed at the Vienna Scientific Cluster (VSC-4).

-
- [1] *Colloidal Magnetic Fluids*, Lecture Notes in Physics, edited by S. Odenbach (Springer-Verlag, Berlin, Heidelberg, 2009), Vol. 763.
 - [2] M. Zrnyi, D. Szabó, and H.-G. Kilian, Kinetics of the shape change of magnetic field sensitive polymer gels, *Polym. Gels Networks* **6**, 441 (1998).
 - [3] R. Weeber, M. Hermes, A. M. Schmidt, and C. Holm, Polymer architecture of magnetic gels: A review, *J. Phys.: Condens. Matter* **30**, 063002 (2018).
 - [4] T. Volkova, V. Böhm, T. Kaufhold, J. Popp, F. Becker, D. Y. Borin, G. Stepanov, and K. Zimmermann, Motion behaviour of magneto-sensitive elastomers controlled by an external magnetic field for sensor applications, *J. Magn. Magn. Mater.* **431**, 262 (2017).
 - [5] S. Frank and P. C. Lauterbur, Voltage-sensitive magnetic gels as magnetic resonance monitoring agents, *Nature (London)* **363**, 334 (1993).
 - [6] R. Weeber, S. Kantorovich, and C. Holm, Deformation mechanisms in 2D magnetic gels studied by computer simulations, *Soft Matter* **8**, 9923 (2012).
 - [7] E. L. Resler, Jr., and R. Rosensweig, Magnetocaloric power, *AIAA J.* **2**, 1418 (1964).

- [8] R. Dreyfus, J. Baudry, M. L. Roper, M. Fermigier, H. A. Stone, and J. Bibette, Microscopic artificial swimmers, *Nature (London)* **437**, 862 (2005).
- [9] J. J. Benkoski, S. E. Bowles, R. L. Jones, J. F. Douglas, J. Pyun, and A. Karim, Self-assembly of polymer-coated ferromagnetic nanoparticles into mesoscopic polymer chains, *J. Polym. Sci., Part B: Polym. Phys.* **46**, 2267 (2008).
- [10] E. M. Furst, C. Suzuki, M. Fermigier, and A. P. Gast, Permanently linked monodisperse paramagnetic chains, *Langmuir* **14**, 7334 (1998).
- [11] E. M. Furst and A. P. Gast, Micromechanics of Dipolar Chains Using Optical Tweezers, *Phys. Rev. Lett.* **82**, 4130 (1999).
- [12] H. Wang, Y. Yu, Y. Sun, and Q. Chen, Magnetic nanochains: A review, *Nano* **06**, 1 (2011).
- [13] H. Wang, A. Mararenko, G. Cao, Z. Gai, K. Hong, P. Banerjee, and S. Zhou, Multifunctional 1D magnetic and fluorescent nanoparticle chains for enhanced MRI, fluorescent cell imaging, and combined photothermal/chemotherapy, *ACS Appl. Mater. Interfaces* **6**, 15309 (2014).
- [14] A. Cebers and K. Erglis, Flexible magnetic filaments and their applications, *Adv. Funct. Mater.* **26**, 3783 (2016).
- [15] G. Cai, S. Wang, L. Zheng, and J. Lin, A fluidic device for immunomagnetic separation of foodborne bacteria using self-assembled magnetic nanoparticle chains, *Micromachines* **9**, 624 (2018).
- [16] K. Ērglis, L. Alberte, and A. Cēbers, Thermal fluctuations of non-motile magnetotactic bacteria in ac magnetic fields, *Magnetohydrodynamics* **44**, 223 (2008).
- [17] D. Fayol, G. Frasca, C. Le Visage, F. Gazeau, N. Luciani, and C. Wilhelm, Use of magnetic forces to promote stem cell aggregation during differentiation, and cartilage tissue modeling, *Adv. Mater.* **25**, 2611 (2013).
- [18] F. Gerbal, Y. Wang, F. Lyonnet, J.-C. Bacri, T. Hocquet, and M. Devaud, A refined theory of magnetoelastic buckling matches experiments with ferromagnetic and superparamagnetic rods, *Proc. Natl. Acad. Sci.* **112**, 7135 (2015).
- [19] B. Evans, A. Shields, R. L. Carroll, S. Washburn, M. Falvo, and R. Superfine, Magnetically actuated nanorod arrays as biomimetic cilia, *Nano Lett.* **7**, 1428 (2007).
- [20] K. Ērglis, R. Livanovičs, and A. Cēbers, Three dimensional dynamics of ferromagnetic swimmer, *J. Magn. Magn. Mater.* **323**, 1278 (2011).
- [21] C. Goubault, P. Jop, M. Fermigier, J. Baudry, E. Bertrand, and J. Bibette, Flexible magnetic filaments as micromechanical sensors, *Phys. Rev. Lett.* **91**, 260802 (2003).
- [22] L. Cohen-Tannoudji, E. Bertrand, L. Bressy, C. Goubault, J. Baudry, J. Klein, J. F. Joanny, and J. Bibette, Polymer bridging probed by magnetic colloids, *Phys. Rev. Lett.* **94**, 038301 (2005).
- [23] H. Singh, P. E. Laibinis, and T. A. Hatton, Rigid, superparamagnetic chains of permanently linked beads coated with magnetic nanoparticles. Synthesis and rotational dynamics under applied magnetic fields, *Langmuir* **21**, 11500 (2005).
- [24] H. Singh, P. E. Laibinis, and T. A. Hatton, Synthesis of flexible magnetic nanowires of permanently linked core-shell magnetic beads tethered to a glass surface patterned by microcontact printing, *Nano Lett.* **5**, 2149 (2005).
- [25] F. Martínez-Pedrero, M. Tirado-Miranda, A. Schmitt, and J. Callejas-Fernández, Formation of magnetic filaments: A kinetic study, *Phys. Rev. E* **76**, 011405 (2007).
- [26] Z. Zhou, G. Liu, and D. Han, Coating and structural locking of dipolar chains of cobalt nanoparticles, *ACS Nano* **3**, 165 (2008).
- [27] J. J. Benkoski, J. L. Breidenich, O. M. Uy, A. T. Hayes, R. M. Deacon, H. B. Land, J. M. Spicer, P. Y. Keng, and J. Pyun, Dipolar organization and magnetic actuation of flagella-like nanoparticle assemblies, *J. Mater. Chem.* **21**, 7314 (2011).
- [28] D. Sarkar and M. Mandal, Static and dynamic magnetic characterization of DNA-templated chain-like magnetite nanoparticles, *J. Phys. Chem. C* **116**, 3227 (2012).
- [29] J. L. Breidenich, M. C. Wei, G. V. Clatterbaugh, J. J. Benkoski, P. Y. Keng, and J. Pyun, Controlling length and areal density of artificial cilia through the dipolar assembly of ferromagnetic nanoparticles, *Soft Matter* **8**, 5334 (2012).
- [30] E. Busseron, Y. Ruff, E. Moulin, and N. Giuseppone, Supramolecular self-assemblies as functional nanomaterials, *Nanoscale* **5**, 7098 (2013).
- [31] J. Byrom, P. Han, M. Savory, and S. L. Biswal, Directing assembly of DNA-coated colloids with magnetic fields to generate rigid, semiflexible, and flexible chains, *Langmuir* **30**, 9045 (2014).
- [32] L. J. Hill and J. Pyun, Colloidal polymers via dipolar assembly of magnetic nanoparticle monomers, *ACS Appl. Mater. Interfaces* **6**, 6022 (2014).
- [33] M. B. Bannwarth, S. Utech, S. Ebert, D. A. Weitz, D. Crespy, and K. Landfester, Colloidal polymers with controlled sequence and branching constructed from magnetic field assembled nanoparticles, *ACS Nano* **9**, 2720 (2015).
- [34] M. M. Maye, D. Nykypanchuk, M. Cuisinier, D. van der Lelie, and O. Gang, Stepwise surface encoding for high-throughput assembly of nanoclusters, *Nat. Mater.* **8**, 388 (2009).
- [35] D. Sun and O. Gang, Dna-functionalized quantum dots: Fabrication, structural, and physicochemical properties, *Langmuir* **29**, 7038 (2013).
- [36] Y. Zhang, F. Lu, K. G. Yager, D. van der Lelie, and O. Gang, A general strategy for the dna-mediated self-assembly of functional nanoparticles into heterogeneous systems, *Nat. Nanotechnol.* **8**, 865 (2013).
- [37] S. Srivastava, D. Nykypanchuk, M. Fukuto, J. D. Halverson, A. V. Tkachenko, K. G. Yager, and O. Gang, Two-dimensional dna-programmable assembly of nanoparticles at liquid interfaces, *J. Am. Chem. Soc.* **136**, 8323 (2014).
- [38] Y. Tian, T. Wang, W. Liu, H. L. Xin, H. Li, Y. Ke, W. M. Shih, and O. Gang, Prescribed nanoparticle cluster architectures and low-dimensional arrays built using octahedral DNA origami frames, *Nat. Nanotechnol.* **10**, 637 (2015).
- [39] W. Liu, J. Halverson, Y. Tian, A. V. Tkachenko, and O. Gang, Self-organized architectures from assorted DNA-framed nanoparticles, *Nat. Chem.* **8**, 867 (2016).
- [40] Y. Xiong, Z. Lin, D. Mostarac, B. Minevich, Q. Peng, G. Zhu, P. A. Sánchez, S. Kantorovich, Y. Ke, and O. Gang, Divalent multilinking bonds control growth and morphology of nanopolymers, *Nano Lett.* **21**, 10547 (2021).
- [41] Z. Lin, H. Emamy, B. Minevich, Y. Xiong, S. Xiang, S. Kumar, Y. Ke, and O. Gang, Engineering organization of dna nanochambers through dimensionally controlled and multi-sequence encoded differentiated bonds, *J. Am. Chem. Soc.* **142**, 17531 (2020).
- [42] A. Cēbers, Dynamics of a chain of magnetic particles connected with elastic linkers, *J. Phys.: Condens. Matter* **15**, S1335 (2003).

- [43] V. P. Shcherbakov and M. Winklhofer, Bending of magnetic filaments under a magnetic field, *Phys. Rev. E* **70**, 061803 (2004).
- [44] A. Cēbers and I. Javitis, Dynamics of a flexible magnetic chain in a rotating magnetic field, *Phys. Rev. E* **69**, 021404 (2004).
- [45] A. Cēbers, Flexible magnetic filaments, *Curr. Opin. Colloid Interface Sci.* **10**, 167 (2005).
- [46] M. Belovs and A. Cēbers, Nonlinear dynamics of semiflexible magnetic filaments in an ac magnetic field, *Phys. Rev. E* **73**, 051503 (2006).
- [47] A. Cēbers and T. Cīrulis, Magnetic elastica, *Phys. Rev. E* **76**, 031504 (2007).
- [48] K. Ērglis, D. Zhulenkova, A. Sharipo, and A. Cēbers, Elastic properties of DNA linked flexible magnetic filaments, *J. Phys.: Condens. Matter* **20**, 204107 (2008).
- [49] A. A. Kuznetsov, Equilibrium properties of magnetic filament suspensions, *J. Magn. Magn. Mater.* **470**, 28 (2019).
- [50] S. Huang, G. Pessot, P. Cremer, R. Weeber, C. Holm, J. Nowak, S. Odenbach, A. M. Menzel, and G. K. Auernhammer, Buckling of paramagnetic chains in soft gels, *Soft Matter* **12**, 228 (2016).
- [51] J. Zhao, D. Du, and S. L. Biswal, Nonlinear multimode buckling dynamics examined with semiflexible paramagnetic filaments, *Phys. Rev. E* **98**, 012602 (2018).
- [52] J. Wei, F. Song, and J. Dobnikar, Assembly of superparamagnetic filaments in external field, *Langmuir* **32**, 9321 (2016).
- [53] S. Kuei, B. Garza, and S. L. Biswal, From strings to coils: Rotational dynamics of DNA-linked colloidal chains, *Phys. Rev. Fluids* **2**, 104102 (2017).
- [54] J. M. Dempster, P. Vázquez-Montejo, and M. O. de la Cruz, Contractile actuation and dynamical gel assembly of paramagnetic filaments in fast precessing fields, *Phys. Rev. E* **95**, 052606 (2017).
- [55] J. J. Cerdà, P. A. Sánchez, D. Lüsebrink, S. S. Kantorovich, and T. Sintes, Flexible magnetic filaments under the influence of external magnetic fields in the limit of infinite dilution, *Phys. Chem. Chem. Phys.* **18**, 12616 (2016).
- [56] P. Vázquez-Montejo, J. M. Dempster, and M. O. de la Cruz, Paramagnetic filaments in a fast precessing field: Planar versus helical conformations, *Phys. Rev. Mater.* **1**, 064402 (2017).
- [57] E. Gauger and H. Stark, Numerical study of a microscopic artificial swimmer, *Phys. Rev. E* **74**, 021907 (2006).
- [58] M. Roper, R. Dreyfus, J. Baudry, M. Fermigier, J. Bibette, and H. A. Stone, On the dynamics of magnetically driven elastic filaments, *J. Fluid Mech.* **554**, 167 (2006).
- [59] M. Roper, R. Dreyfus, J. Baudry, M. Fermigier, J. Bibette, and H. A. Stone, Do magnetic micro-swimmers move like eukaryotic cells? *Proc. R. Soc. London A* **464**, 877 (2008).
- [60] O. Philippova, A. Barabanova, V. Molchanov, and A. Khokhlov, Magnetic polymer beads: Recent trends and developments in synthetic design and applications, *Eur. Polym. J.* **47**, 542 (2011).
- [61] O. S. Pak, W. Gao, J. Wang, and E. Lauga, High-speed propulsion of flexible nanowire motors: Theory and experiments, *Soft Matter* **7**, 8169 (2011).
- [62] P. A. Sánchez, E. S. Pyanzina, E. V. Novak, J. J. Cerdà, T. Sintes, and S. S. Kantorovich, Supramolecular magnetic brushes: The impact of dipolar interactions on the equilibrium structure, *Macromolecules* **48**, 7658 (2015).
- [63] S. L. Biswal and A. P. Gast, Micromixing with linked chains of paramagnetic particles, *Anal. Chem.* **76**, 6448 (2004).
- [64] T. Yang, T. O. Tasci, K. B. Neeves, N. Wu, and D. W. Marr, Magnetic microlasos for reversible cargo capture, transport, and release, *Langmuir* **33**, 5932 (2017).
- [65] M. T. López-López, P. Kuzhir, and G. Bossis, Magnetorheology of fiber suspensions. I. Experimental, *J. Rheol.* **53**, 115 (2009).
- [66] D. Mostarac, P. A. Sánchez, and S. Kantorovich, Characterisation of the magnetic response of nanoscale magnetic filaments in applied fields, *Nanoscale* **12**, 13933 (2020).
- [67] D. Mostarac, E. Novak, P. A. Sánchez, and S. Kantorovich, The impact of magnetic field on the conformations of supracolloidal polymer-like structures with super-paramagnetic monomers, *J. Mol. Liq.* **305**, 112761 (2020).
- [68] D. Mostarac, Y. Xiong, O. Gang, and S. Kantorovich, Nanopolymers for magnetic applications: How to choose the architecture? *Nanoscale* **14**, 11139 (2022).
- [69] D. Mostarac and S. S. Kantorovich, Rheology of a nanopolymer synthesized through directional assembly of DNA nanochambers, for magnetic applications, *Macromolecules* **55**, 6462 (2022).
- [70] P. Tierno, R. Muruganathan, and T. M. Fischer, Viscoelasticity of dynamically self-assembled paramagnetic colloidal clusters, *Phys. Rev. Lett.* **98**, 028301 (2007).
- [71] P. Garstecki, P. Tierno, D. B. Weibel, F. Sagués, and G. M. Whitesides, Propulsion of flexible polymer structures in a rotating magnetic field, *J. Phys.: Condens. Matter* **21**, 204110 (2009).
- [72] S. N. Innes-Gold, I. L. Morgan, and O. A. Saleh, Surface-induced effects in fluctuation-based measurements of single-polymer elasticity: A direct probe of the radius of gyration, *J. Chem. Phys.* **148**, 123314 (2017).
- [73] F. Weik, R. Weeber, K. Szuttor, K. Breitsprecher, J. de Graaf, M. Kuron, J. Landsgesell, H. Menke, D. Sean, and C. Holm, Espresso 4.0 – An extensible software package for simulating soft matter systems, *Eur. Phys. J.: Spec. Top.* **227**, 1789 (2019).
- [74] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, New York, 2017).
- [75] G. E. Uhlenbeck and L. S. Ornstein, On the theory of the Brownian motion, *Phys. Rev.* **36**, 823 (1930).
- [76] D. C. Rapaport, *The Art of Molecular Dynamics Simulation* (Cambridge University Press, Cambridge, 2004).
- [77] E. V. Novak, E. S. Pyanzina, P. A. Sánchez, and S. S. Kantorovich, The structure of clusters formed by Stockmayer supracolloidal magnetic polymers, *Eur. Phys. J. E* **42**, 158 (2019).
- [78] B. Smit, C. Williams, E. Hendriks, and S. D. Leeuw, Vapour-liquid equilibria for Stockmayer fluids, *Mol. Phys.* **68**, 765 (1989).
- [79] M. E. van Leeuwen and B. Smit, What makes a polar liquid a liquid? *Phys. Rev. Lett.* **71**, 3991 (1993).
- [80] A. Z. Panagiotopoulos, Direct determination of fluid phase equilibria by simulation in the Gibbs ensemble: A review, *Mol. Simul.* **9**, 1 (1992).
- [81] M. J. Stevens and G. S. Grest, Structure of soft-sphere dipolar fluids, *Phys. Rev. E* **51**, 5962 (1995).

- [82] D. Adams and E. Adams, Static dielectric properties of the Stockmayer fluid from computer simulation, [Mol. Phys. **42**, 907 \(1981\)](#).
- [83] E. Novak, E. Pyanzina, D. Rozhkov, M. Ronti, J. Cerdà, T. Sintes, P. Sánchez, and S. Kantorovich, Suspensions of supracolloidal magnetic polymers: Self-assembly properties from computer simulations, [J. Mol. Liq. **271**, 631 \(2018\)](#).
- [84] A. O. Ivanov and O. B. Kuznetsova, Magnetic properties of dense ferrofluids: An influence of interparticle correlations, [Phys. Rev. E **64**, 041405 \(2001\)](#).