



## Research articles

## The influence of the magnetic filler concentration on the properties of a microgel particle: Zero-field case

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## ABSTRACT

In this contribution we present a molecular dynamics study of a microgel colloidal particle filled with magnetic nanobeads. The microgel is constructed of crosslinked polymer chains, some beads of which are magnetic. We vary the concentration of magnetic particles and the degree of crosslinking in the microgel to analyse the influence of both factors on the radius of gyration, microstructure and the initial magnetic susceptibility of our soft magnetic colloid. We show that even for a loosely crosslinked microgel, the concentration of magnetic filler must be rather high in order for the magnetic dipolar interactions to affect the shape and the internal structure of the soft colloid.

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## 1. Introduction

The combination of magnetic particles of nano- or/and micrometer size and a polymer matrix gave rise to a new class of soft materials [1–5]. Among them, the most actively studied are magnetic gels, in which the polymer matrix is swollen by a carrier liquid [6–13], and soft magnetic elastomers, also known as magnetorheological elastomers, that are magnetic rubber-like dry materials [5,14–20].

Characteristic to these materials, the coupling between the magnetic interactions and the deformation of the polymer matrix makes them very promising for various technological applications, such as adaptive damping devices, vibrational absorbers, artificial muscles and many others [16,21–26]. However, despite the growing scientific and industrial interest that magnetic gels and elastomers are attracting, their properties are still far from being completely understood.

Magnetic gels and elastomers have been studied to date using different strategies. Computer simulations of these systems are usually based on coarse-grained approaches: magnetic particles are represented as beads with point magnetic dipoles, whereas the polymer matrix is either modelled implicitly [27,28] or represented with different levels of detail [29–38]. Along with computer simulations, several works employ continuum analytical theories

[39–42] to describe the magneto-elastic coupling of these materials.

Among magnetic soft materials, one class of the most novel and interesting systems are the ones known as microgel particles or soft colloids. These particles are formed by polymers crosslinked in a network whose size is of the order of 10 nm to 1 μm. The synthesis of microgels is usually based on polymerisation techniques with added crosslinkers [43,44]. Crosslink density influences both the particle's internal structure and its swelling properties. Since swelling and deswelling are determined by the balance between the elastic forces of crosslinkers and the rest of interactions in the system, it can be controlled by different factors like, for example, temperature, solvent quality or, when the microgel particle carries embedded magnetic beads, external magnetic fields [43–48]. This ability to change their size in response to external perturbations makes microgels advanced materials with potential for many applications [49–52,43]. In addition, self-assembly of concentrated microgels can be tuned by change or additionally imposed electric fields [53–56]. In particular, microgels with embedded magnetic particles [45] are interesting materials from the point of view of both, technological applications and fundamental knowledge, and are the main subject of this work.

In this study we analyse the influence of interparticle magnetic interactions on the shape, microstructure and magnetic susceptibility of a microgel particle by means of computer simulations. We thoroughly study microgels with different degrees of crosslinking and containing different amount of permanently magnetised particles. We also vary the strength of magnetic interparticle inter-

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actions, analysing the effect of such parameters on the gyration radii of the microgels and their initial susceptibility. Finally, we also extract information about the formation of clusters of magnetic particles in the system.

The manuscript is organised as follows: In the next section we introduce the microgel model and our simulation approach. The main results are provided in Section 3. Finally, the summary of the work and the outlook can be found in Conclusions.

## 2. Model and methods

We chose a coarse-grained modelling approach for microgel particles based on a bead-spring explicit representation of the polymer matrix [57]. In our model, a microgel particle is composed of  $N_p = 6$  linear polymer chains. Each polymer contains  $N_m = 100$  monomers of diameter  $\sigma = 1$ . The monomers repel each other via a soft-core Weeks-Chandler-Andersen potential:

$$\beta U_{WCA}(r) = \begin{cases} 4 \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4} \right], & r \leq r_c \\ 0, & r \geq r_c \end{cases} \quad (1)$$

with a cut-off distance  $r_c = 2^{1/6}\sigma$ , being  $r$  the distance between the particle centres and  $\beta = 1/k_B T$  the Boltzmann factor. The monomers are bonded in polymer chains by means of FENE springs, defined by the following potential:

$$\beta U_{FENE}(r) = -\frac{1}{2}\epsilon_f \ln \left[ 1 - \left(\frac{r}{r_f}\right)^2 \right] \quad (2)$$

where  $r_f = 1.5\sigma$  is the maximal bond extension and  $\epsilon_f = 22.5$  is the interaction strength.

In order to create a crosslinked polymer network, we place the polymers inside a spherical shell with a radius equivalent to the end-to-end distance of a single non-constrained polymer,  $\sigma N_m^{0.59}$ , and add different amounts of cross-links,  $N_{links} = \{20, 100, 200\}$ , as bonds between selected pairs of particles. These bonds are represented by the harmonic potential

$$\beta U_h(r) = -\frac{1}{2}K(r - \sigma)^2, \quad (3)$$

where  $K = 10$  is the spring constant. The candidates to form cross-linked pairs necessarily belong to different polymers and are chosen randomly among the pairs separated by the distance not greater than  $1.2\sigma$ . If there are not enough candidates to form the desired number of pairs separated by this distance, we gradually increase this distance by  $0.1\sigma$  and again look for the candidates to link. After crosslinking, we remove the spherical shell and let the microgel relax. In this manner, we obtain microgels whose degree of crosslinking corresponds to 7%, 33% and 67% to the total number of monomers comprising the microgel,  $N = N_p N_m$ .

In order to fill the microgel with magnetic particles, we replace a certain number of monomers along the polymer chains,  $N_{mag}$ , with magnetic dipolar particles. This replacement is performed randomly to ensure independence from the initial configuration. The diameter and the soft-core and bonding interactions of the magnetic beads are identical to the ones defined for the polymer monomers, with the only addition of a permanent magnetic moment,  $\boldsymbol{\mu}$ , located at the particle center. The magnetic moment can freely rotate in three-dimensional space. Therefore, any pair of magnetic particles,  $i$  and  $j$ , experience a dipole-dipole interaction defined by

$$\beta U_{dd}(\mathbf{r}_{ij}, \boldsymbol{\mu}_i, \boldsymbol{\mu}_j) = \frac{\mu_0}{4\pi} \left[ \frac{(\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j)}{r_{ij}^3} - \frac{3(\boldsymbol{\mu}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right], \quad (4)$$

where  $\mu_0$  is the vacuum permeability. The strength of this potential is characterised by the dipolar coupling parameter,  $\lambda = \beta\mu_0\mu^2/4\pi\sigma^3$ , that is the ratio of magnetic energy per particle in the minimum configuration to the thermal energy. After filling the microgel with magnetic particles, we again equilibrate it.

To elucidate how much the dipolar interactions affect the microgel conformations, we varied the fraction of magnetic particles,  $v_{mag} = N_{mag}/N$ , from 0.5% to 10%. In addition, we changed the strength of the dipolar interactions in a broad range, corresponding to values of the dipolar coupling parameter  $\lambda = 1, 2, \dots, 8$ .

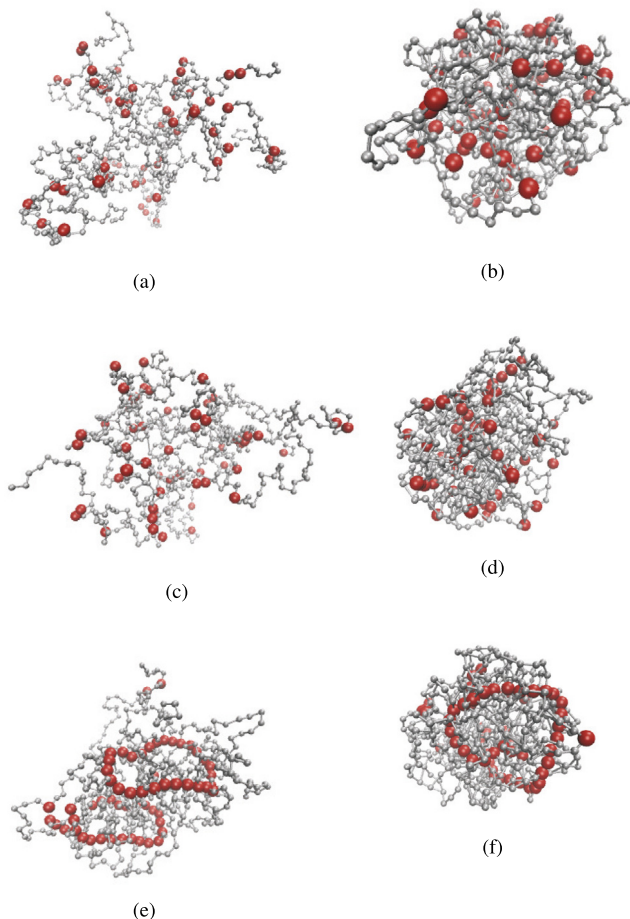
We performed molecular dynamics simulations of the microgels with the simulation package ESPReso [58]. To integrate the equations of motion, we employed a velocity Verlet integrator with a fixed time step  $\Delta t = 0.01$ . The dimensionless temperature of the system in simulations was kept constant,  $T^* = 1$ , by means of a Langevin thermostat with dimensionless friction equal to unity. The simulations started by placing the polymers inside the spherical shell and warming up the system during  $10^7$  integration steps. Then, the crosslinking procedure was carried out and the spherical shell was removed. After this, the system was first equilibrated for  $10 \times 10^8$  integration steps and then measurements were obtained in a last cycle of  $10 \times 10^6$  steps. Finally, we sampled each set of parameters with 10 independent runs using different initial configurations.

It is worth mentioning that our crosslinking routine is constructed in order to efficiently build a spherical microgel particle with embedded magnetic beads. Being a numerical trick, it is not aimed at reproducing any chemical process. The final microgel, however, represents a rather realistic coarse-grained approximation of the systems found in Refs. [43–48]. Note that having six chains in the simulation does not mean that our model captures the physics of microgels made only of six chains. The model is rather general and it helps understanding possible effects of magneto-elastic coupling in soft matter, albeit neglecting all molecular detail.

## 3. Results and discussions

Fig. 1 shows some examples of microgel configurations for different degrees of crosslinking and  $\lambda$ . Microgels with more crosslinkers are more compact and hold a more spherical shape, whereas the microgels with few crosslinkers are rather fuzzy. The increase in the strength of dipolar interactions, defined by  $\lambda$ , leads to the formation of chains of magnetic particles. At high  $\lambda$ , the chains formed in microgels with few crosslinkers tend to close into rings, as a ring is the ground state for dipolar spheres [59–62] and the network is not rigid enough to prevent the closure of the chains.

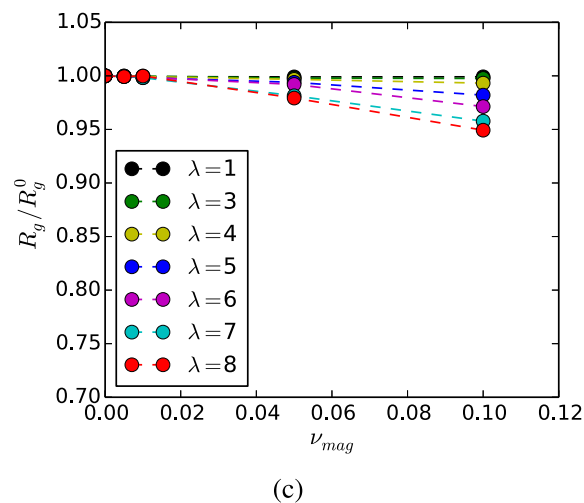
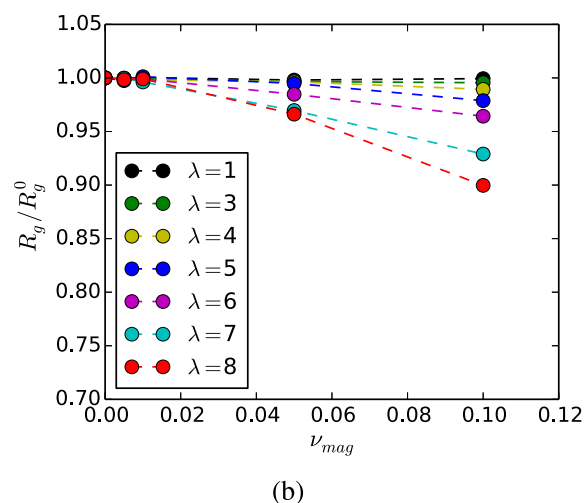
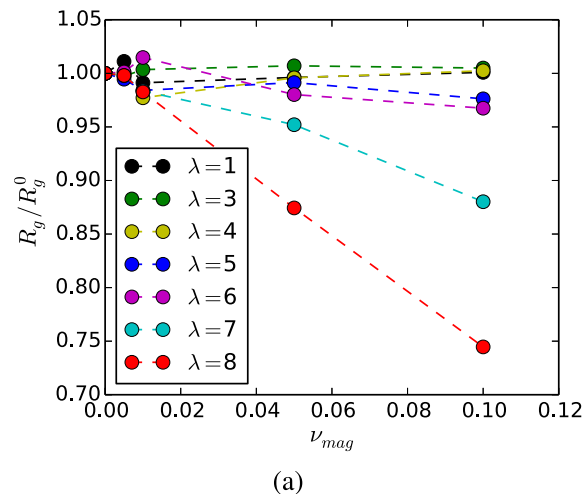
Fig. 2 shows the radius of gyration of the microgels,  $R_g$ , as a function of the fraction of magnetic particles. This parameter, scaled with the value corresponding to analogous non-magnetic microgels, allows us to estimate the influence of the degree of crosslinking and magnetic particles on the characteristic size of the microgels. One can observe that the degree of crosslinking of the polymer network strongly affects the size of the microgels. The less crosslinked the polymer network is, the bigger are the changes in the size of the microgels with the increase of the role of the magnetic interactions, either led by the increase of the fraction of magnetic particles or by the increase of  $\lambda$ . The increase of the magnetic particle fraction leads to a decrease in size of the microgels. However, the strength of dipolar interactions should be rather high ( $\lambda > 4$ ) in order to make this change in size significant, especially for microgels with a high degree of crosslinking (see Fig. 2c).



**Fig. 1.** Simulation snapshots of the microgels with magnetic particles. (a)  $N_{\text{cros}} = 20, \lambda = 1$ ; (b)  $N_{\text{cros}} = 200, \lambda = 1$ ; (c)  $N_{\text{cros}} = 20, \lambda = 5$ ; (d)  $N_{\text{cros}} = 200, \lambda = 5$ ; (e)  $N_{\text{cros}} = 20, \lambda = 8$ ; (f)  $N_{\text{cros}} = 200, \lambda = 8$ . Nonmagnetic particles are represented in gray. The magnetic particles, which fraction is kept constant at  $\nu_{\text{mag}} = 0.1$ , are depicted as red spheres of bigger size than the actual one to distinguish them from the nonmagnetic ones.

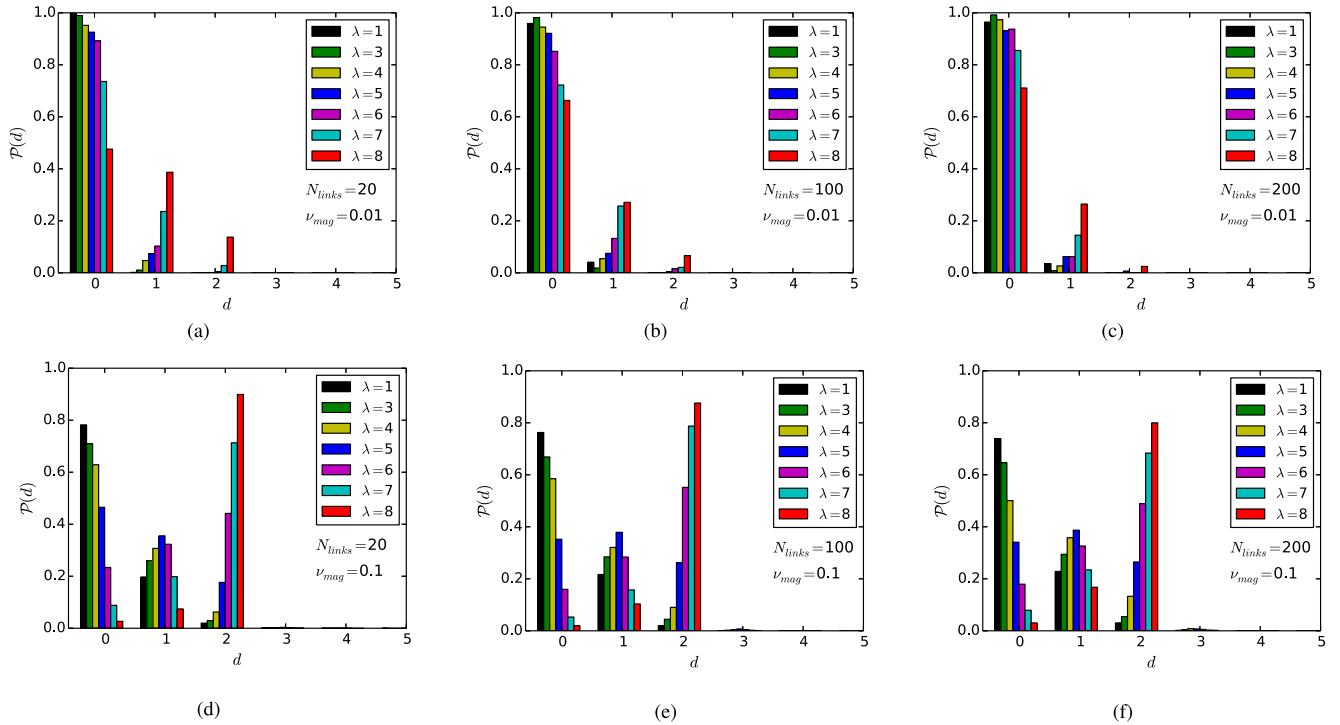
To analyse the self-assembly of the magnetic particles into chains and rings, we compute the probability  $\mathcal{P}(d)$  of finding  $d$  neighboring magnetic particles in a vicinity  $\delta r \leq 1.2\sigma$  from a given magnetic particle. The result of this calculation is depicted in Fig. 3. If the microgels contain few magnetic particles (see Fig. 3a–c), they tend to not cluster, independently of the degree of crosslinking of the polymer network. Only extremely high dipolar interactions  $\lambda \approx 8$  can force them to form pairs. The situation changes when we increase the number of magnetic particles by a factor of 10 (see Fig. 3d–f): it becomes more likely to find magnetic particles in a cluster as we increase  $\lambda$ . Moreover, at high  $\lambda > 6$ , the vast majority of magnetic particles are most likely to have two neighbors. This means that dipolar interactions are high enough to allow the formation of long chains regardless the arrangement of magnetic particles in the polymer network and its degree of crosslinking. Such long chains are observed in simulations for both microgels with few and many crosslinkers at high  $\lambda$  (see the simulation snapshots in Fig. 1e and f).

We have also measured the initial magnetic susceptibility of the microgels,  $\chi_0 = \rho_{\text{mag}} (\langle \mathbf{m}^2 \rangle - \langle \mathbf{m} \rangle^2) / k_B T$  [63], that is depicted in Fig. 4. Here,  $\mathbf{m} = \sum_{i=1}^{N_{\text{mag}}} \boldsymbol{\mu}_i / N_{\text{mag}}$  and  $\rho_{\text{mag}}$  is the number density of the magnetic particles. The initial susceptibility grows with the increase of the magnetic particles in the system and rises as the microgel becomes more compact, i.e., for highly crosslinked poly-

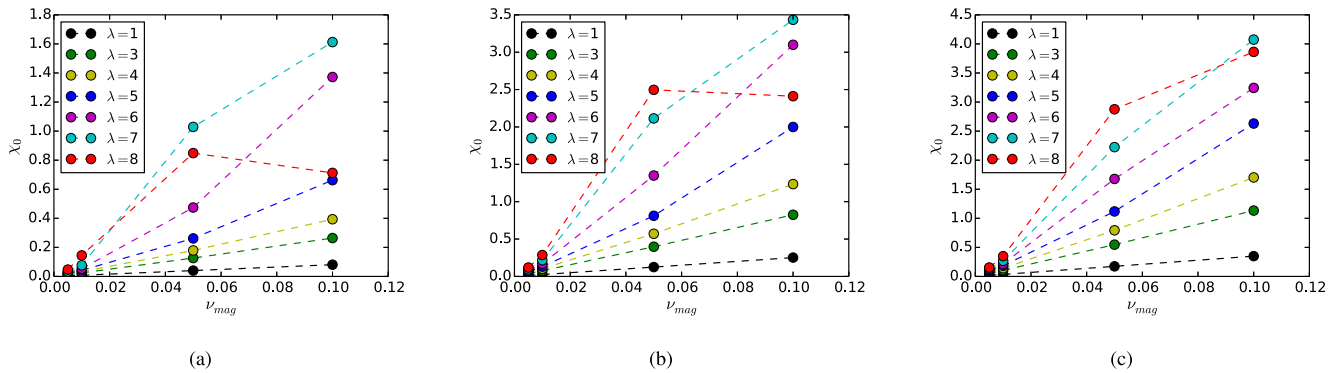


**Fig. 2.** The radius of gyration of microgels with embedded magnetic particles rescaled by the corresponding radius of gyration of non-magnetic microgels  $R_g/R_g^0$  vs the fraction of magnetic particles  $\nu_{\text{mag}}$  at different strength of dipolar interactions  $\lambda$ . (a) microgels with few crosslinkers  $N_{\text{links}} = 20$ , (b) microgels with  $N_{\text{links}} = 100$ , (c) microgels with  $N_{\text{links}} = 200$ .

mer network, when compared to weakly crosslinked microgels at the same  $\lambda$ . The crosslinkers tend to decrease the distance between the magnetic particles, facilitating the chain formation as Fig. 3 confirms. However, having many magnetic particles embedded in



**Fig. 3.** The probability  $\mathcal{P}(d)$  of finding  $d$  neighboring magnetic particles in a vicinity  $\delta r \leq 1.2\sigma$  from a given magnetic particle. The plots (a)–(c) in the upper row are obtained for microgels with magnetic particle fraction  $\nu_{mag} = 0.01$ , the plots (d)–(f) in the lower row are obtained for microgels with magnetic particle fraction  $\nu_{mag} = 0.1$ . The plots in the first column (a) and (d) correspond to  $N_{links} = 20$ ; the plots in the second column (b) and (e) correspond to  $N_{links} = 100$ ; the plots in the third column (c) and (f) correspond to  $N_{links} = 200$ .



**Fig. 4.** The initial magnetic susceptibility  $\chi_0$  of the microgels vs the fraction of magnetic particles  $\nu_{mag}$  at different strength of dipolar interactions  $\lambda$ : (a)  $N_{links} = 20$ , (b)  $N_{links} = 100$ , (c)  $N_{links} = 200$ .

the microgels results in long chain formation at high  $\lambda = 8$ . These chains develop through the microgel network and try to close into rings. Although it is not always possible for them to form totally closed structures due to the tightly crosslinked network, nearly closed structures also contribute to decrease the total magnetic moment of the system and, therefore, lead to a decrease of the initial susceptibility (see the data for  $\lambda = 8$  labeled in red in Fig. 4).

**4. Conclusion**

In this paper, we studied microgels with embedded magnetic particles in its polymer network by means of molecular dynamics computer simulations. We showed that the size of microgels decreases with growing strength of dipolar interactions and that microgels can be much easier deformed when they are loosely crosslinked. However, regardless the degree of crosslinking, the

growth in the fraction of magnetic particles leads to the formation of long chains of magnetic particles at high  $\lambda$ . On the other hand, the polymer network, especially when highly crosslinked, hinders the closure of the chains into rings. In this case, the magnetic particles form nearly closed structures that result in a strong decrease of the initial magnetic susceptibility of such systems. The later has to be taken into account in the design of soft magnetic materials, especially when a high magnetic response is desired.

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