

# The effect of magnetic nanoparticle concentration on the structure organisation of a microferrogel

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**Abstract.** Coarse-grained molecular dynamics simulation is applied to study the structural response of micro-sized magnetopolymer objects – microferrogels (MFG). The results for MFGs with different magnetic properties and concentrations of magnetic filler nanoparticles are analysed to detect the transition between non-aggregated configurations and the states with pronounced chains. The nanoparticles are assumed to be either magnetically isotropic or to possess infinite magnetic anisotropy. It is shown that, depending on the type of the particle anisotropy, an applied field in rather different ways affects the MFG structure and shape. Diagrams describing the degree of aggregation as a function of the parameter of the interparticle magnetodipolar interaction and concentration are presented. In particular, it is found that in the case of infinitely anisotropic nanoparticles the aggregation transitions undergoes via a non-trivial scenario. The effect of the structure transformations on the volume change of the MFG objects is studied as well.

## 1. Introduction

Microferrogels (magnetic microgels, microscopic ferrogels, MFGs) are isolated soft polymers objects with typical sizes in the range of 0.1-10  $\mu\text{m}$  containing embedded magnetic nanoparticles (NPs); typical NP materials are magnetite and cobalt ferrite [1, 2]. Strong coupling between the magnetic NPs and the polymer mesh, in which the NPs take on the role of cross-linkers, ensures the dependence of mechanical and structural properties of a MFG object on the external magnetic field. Therefore, an inherent property of MFGs is the remote control over their structure, volume and shape. Such a possibility of field-aided manipulations is very important, for example, for drug delivery, drug release and other biomedical applications [3, 4, 5, 6].

As it was shown in Refs. [7, 8], structure (i.e., chain formation), magnetisation and volume changes due to application of an external uniform magnetic field depend on the type of uniaxial magnetic anisotropy of NPs. However, the above-cited works were focused exclusively on highly-filled samples with strong dipolar magnetic interaction between NPs. Hereby we continue molecular dynamics study of magneto-structural and magneto-mechanical responses of



individual MFGs and analyse the dependence of structural properties of MFGs on concentration of the magnetic filler particles as well as on the parameter of interparticle interaction.

## 2. Model

We use two models of nanoparticles which correspond to the limiting cases of their internal magnetic anisotropy. In the first case, it is a particle whose magnetic moment is entirely free to rotate inside its body, i.e., the particle has zero anisotropy and, thus, is perfectly magnetically soft. The other model implies that the magnetic moment is tightly “frozen” in the particle body, i.e., the particle is absolutely magnetically hard, its magnetic anisotropy is infinite. To distinguish between those two situations, we define parameter  $\sigma = E_A/k_B T$  that relates the magnetic anisotropy energy to thermal one. Therefore, the considered particles have either  $\sigma = 0$  or  $\sigma = \infty$ .

The model MFG samples generated for simulations contain the particles of the same  $\sigma$ , which make the nodes of a simple cubic lattice constructed of bead-spring polymer strands. In the framework of coarse-grained molecular dynamics, each strand is constructed of a chain of structure units (polymer blobs) which, but conditionally, are termed as “monomers”. Each monomer has two neighbours, to which it is linked by central-bonded harmonic potentials equivalent to simple springs with equal rigidity and equilibrium lengths. In an MFG, the end monomers of some strands are attached in the same way to the NPs. Under such linking, the MFG subsystems turn out to be always coupled, while, as shown below, the parameter  $\sigma$  determines the extent of that coupling.

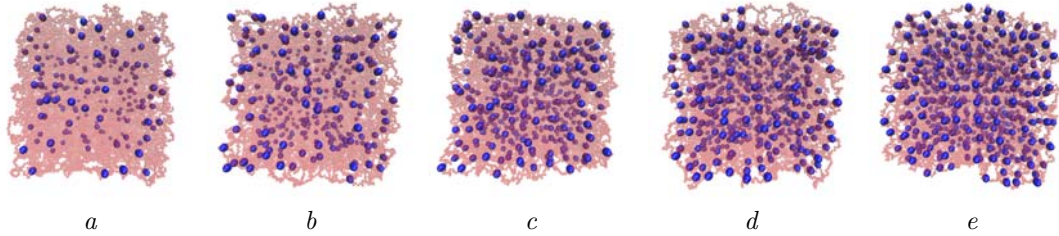
The concentration of magnetic filler in the samples is defined on the basis of the number of the lattice (mesh) nodes occupied by the particles. The residual fraction of the nodes are the sites where the polymer chains are connected only with each other; in simple cubic lattice this means a “meeting point” of six chains.

The samples with different fractions of magnetic filler were generated in the following way. First a “pre-initial” configuration, being a simple cubic lattice with  $10^3$  nodes, is used, where the lattice period is equal to the contour length of the polymer strand. In our simulations all the strands were equal and comprised 12 identical blobs (monomer). To make the polymer object sufficiently soft and to provide mobility for the magnetic particles, the size of the monomer is taken three times smaller than that of the NP., and no angular rigidity is introduced.

As soon as the magnetic phase concentration  $c$  for a given simulation is defined, then the numbers of the occupied and particle-free nodes are calculated as  $N_p = cN_{tot}$ , where  $N_{tot}$  is the total number of nodes in the sample. Thus determined amount of NPs is distributed at random over all the nodes.

After this “pre-initial” configuration of the sample is assembled, it is subjected to thermalisation by setting it in the thermostat of given temperature and letting the polymer strands to fluctuate. This thermalisation stage is also preliminary, as during it the NPs are treated as non-magnetic, and when performing simulation, only steric potentials for the structure units (blobs and NPs altogether) and the bonding potentials of the blob strands are taken into account. To allow for the stochastic nature of the thermostat action as well as for random distribution of NPs over the mesh nodes, the averaging over several implementations of the same sample is carried out. The snapshots of MFG samples with different particle concentrations are shown in Fig. 1.

Upon having attained the thermalised state, the magnetodipole interaction between the NPs, all of which are assumed to bear equal permanent magnetic moments  $\mu$  and be of the same diameter  $d_{np}$ , is turned on. The intensity of this interaction is characterised by the nondimensional parameter  $\lambda = \mu^2/(d_{np}^3 k_B T)$  that relates the magnetodipole energy of two particles in tight contact to thermal energy. Then the final stage of simulation is commenced: the equation of motion of all the elements of the MFG sample are integrated (with all the



**Figure 1.** (Colour online) Thermalised configurations with different number of nodes occupied by NPs; 20% of nodes (*a*), 35% (*b*), 50% (*c*), 65% (*d*), 80% (*e*).

constraints and random forces and torques) until the energetically stationary state is attained.

### 3. Results and discussion

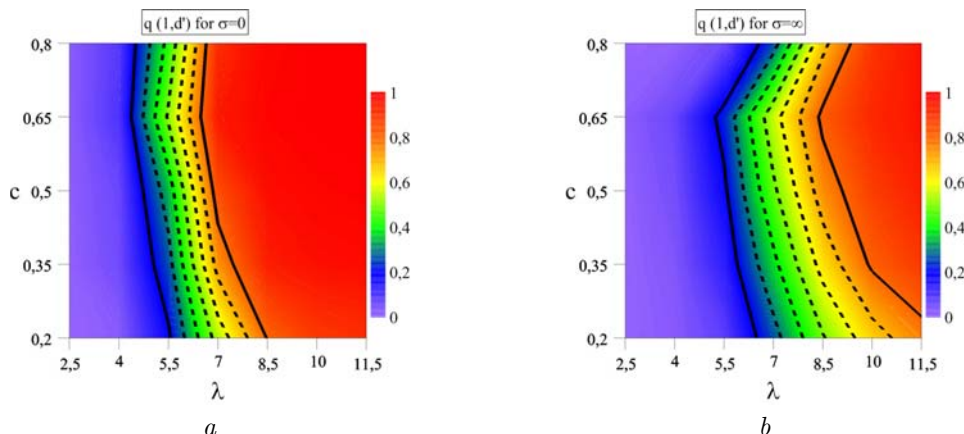
In this work we focus on the structures induced in the two afore-mentioned types of MFGs (with  $\sigma = 0$  or  $\infty$ ) in the absence of external magnetic field. For that, we use an indicator function  $q(j, \tilde{d})$  introduced in Ref. [7]. It renders the fraction of NPs possessing at least  $j$  neighbours whose center-to-center distances are less or equal the value  $\tilde{d}$  that is chosen quite close to  $d_{np}$ ; in our calculations we set  $\tilde{d} = 1.1d_{np}$ . Therefore, the values  $q(1, \tilde{d})$ ,  $q(2, \tilde{d})$ , and  $q(3, \tilde{d})$  yield the number of particles which have at least one, two or three nearest neighbours, respectively.

As a general fact, we remark that in all the MFGs studied, the value of  $q(3, \tilde{d})$  turns out to be virtual zero that points out the absence of multi-particle clusters and/or branched NP aggregates. In other words, practically all the forming aggregates are chains.

In all the simulations we find that for a given concentration, the value of  $q(1, \tilde{d})$  that reflects the presence of any aggregates (including pair clusters) grows with the increase of the dipolar interaction  $\lambda$ . As shown in Fig. 2, indicator  $q(1, \tilde{d})$  changes mostly fast (from 0.2 to 0.8) in a relatively narrow interval of  $\lambda$ . Because of that, one may interpret the occurring change of the MFG as a structure transition from a nearly homogeneous (the majority of the particles are single) to the aggregated state where the majority of the particles are united in chains. It seems reasonable to associate the finite width of this interval (at  $c = \text{const}$ ) with the distributions of (i) the local interparticle distances and (ii) the local effective elasticity of the mesh in a given realisation of the MFG sample; fluctuations of those distributions in different realisations of the sample should also contribute to smearing of the transition region. We remark that in a given MFG the only way to initiate the above-discussed transition is to move parameter  $\lambda$  by varying temperature. However, temperature is a factor that influences all the properties of a gel that has to be taken into account for real systems.

From the diagrams of Fig. 2 it is seen that the transition zones are bow-shaped (leftward inflected) independently of the type of the particle anisotropy. Therefore, in any of MFGs under consideration the aggregation transition requires minimal intensity of the interparticle interaction at moderate concentrations of the magnetic phase, while to induce the same transition at either low or high concentration one needs to enhance the value of  $\lambda$ .

Note that the bow-shaped configuration of the transition zones in Fig. 2 is due to two different effects. At the low-concentration end it is entailed by the fact that mean interparticle distances in such MFGs are large. As the magnetodipole coupling decreases rather fast with the distance, to provide a sufficient attraction force at given temperature it is necessary to enhance the reference value of the interaction, i.e., to increase  $\lambda$  in fact is. In a system with high NP concentration, the factor impeding aggregation is most probably the self-averaging of the local field. Mutual



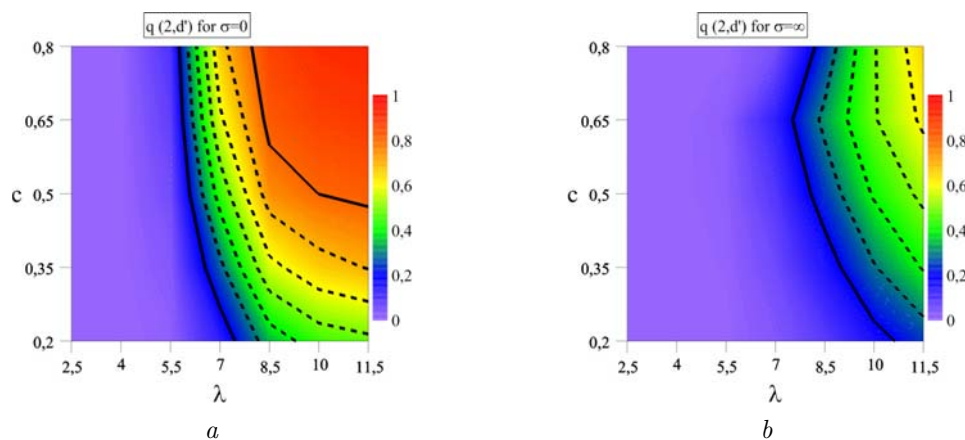
**Figure 2.** (Colour online) Dependence of the aggregation indicator  $q(1, \tilde{d})$  on concentration  $c$  and parameter of magnetodipolar interaction  $\lambda$  for: (a) magnetically isotropic particles  $\sigma = 0$  and (b) magnetically anisotropic particles  $\sigma = \infty$ . Solid black lines are isolines of  $q(1, \tilde{d}) = 0.2$  and 0.8, dashed black lines correspond to intermediate values of  $q(1, \tilde{d})$ .

attraction of a given pair of particles is slackened by the fields induced by the surrounding ones which are positioned quite close to the pair. To overcome this screening, the enhanced pairwise interaction is required.

Comparison of the diagrams for MFGs with  $\sigma = 0$  and  $\sigma = \infty$  in Fig. 2 reveals that for anisotropic particles the aggregation is notably hampered. To understand the origin of this effect, it suffices to recall that in a system with  $\sigma = \infty$  the orientation of the NP magnetic moment is strongly coupled to the positions of the blob chains grafted to the NP surface. Therefore, to point its magnetic moment along the direction optimising the magnetodipole interaction with other particles, the given one has to move its mesh environment. Evidently, this displacement requires some extra energy in comparison with the case of magnetically soft NP where the internal rotations of the magnetic moment do not cost any energy. This causes apparent difference between Figs. 2 a and b: the enhanced width of the transition “band” and a notable enhancement of the reference values of  $\lambda$  corresponding to the aggregation transition for any given concentration. On this basis, one concludes that, if to take two MFG samples possessing the same concentration and same magnitude of parameter of  $\lambda$ , then under zero external field the sample with anisotropic particles would display a considerably lower degree of aggregation.

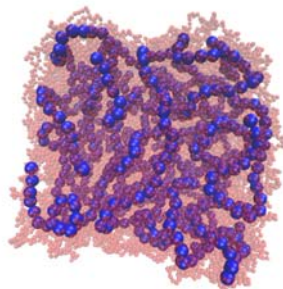
The above-described character of the transition from non-aggregated to chained state in MFGs is confirmed by the plots of indicator  $q(2, \tilde{d})$ , see Fig. 3. This function characterise the fraction of NPs which are incorporated in chains comprising at least three-particle clusters.

Aggregation of the particles resulting in formation of “coil” structures, see Fig. 3, affects the polymer conformations in the MFGs. By that, it entails the change of the sample density and, thus, its volume  $V$ . For MFGs with magnetically isotropic filler the volume change behaves expectably: the greater the magnetodipolar interaction, i.e., the higher the degree of chaining, the larger is the relative “volume defect”  $\Delta V = (V - V_0)/V_0$  where  $V_0$  is the volume of a thermalised sample with the switched off magnetic interactions. Under growth of the interparticles magnetic forces, i.e., of parameter  $\lambda$ , the volume defect  $\Delta V$  of such a sample saturates due to pure steric reasons. This is illustrated by Fig. 5a, see the dashed lines there.



**Figure 3.** (Color online) Dependence of the aggregation indicator  $q(2, \tilde{d})$  on concentration  $c$  and parameter of magnetodipolar interaction  $\lambda$  for: (a) magnetically isotropic particles  $\sigma = 0$  and (b) magnetically hard particles  $\sigma = \infty$ . Solid black lines are isolines of  $q(2, \tilde{d}) = 0.2$  and  $0.8$ , dashed black lines correspond to intermediate values of the degree of aggregation.

Note that in this case the magnitude of  $\Delta V$  increases monotonously with the NP concentration. We remark also that the behaviour reflected by Fig. 5a to a good extent correlates with the diagram of indicator  $q(2, \tilde{d})$  in Fig. 3a.

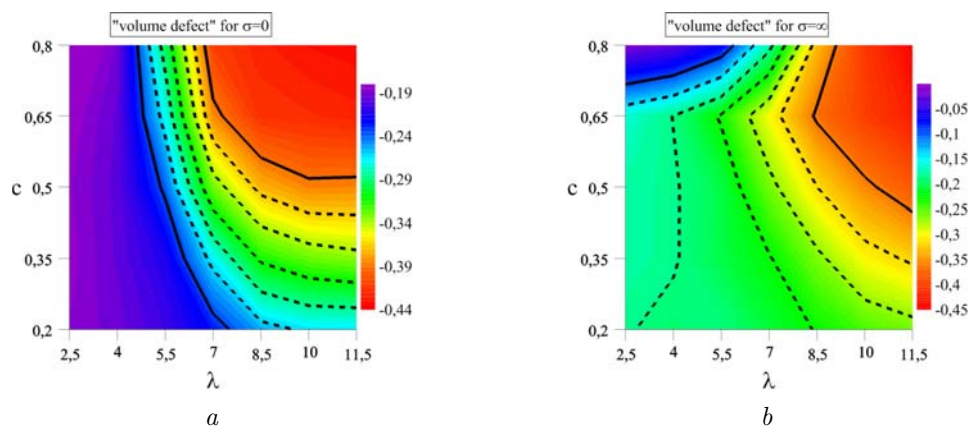


**Figure 4.** (Colour online) “Coil”-like aggregated configuration of an MFG that is densely filled ( $c = 0.8$ ) with magnetically soft particles ( $\sigma = 0$ ) possessing high dipolar moments ( $\lambda = 11.5$ )

For the model MFG with infinitely hard particles, the reference interval of the volume defect to the smaller value side, cf. colour scales in Figs. 5a and 5b. The cause of that is the necessity for the anisotropic particles to overcome rotational constraints imposed by the polymer strands in addition to the translational ones. Indeed, for the interaction parameters from  $\lambda = 2.5$  to about  $\lambda = 7.0$ , the magnitude of  $\Delta V$  grows rather slowly for low and moderate concentrations that implies that the distortion of the polymer in the vicinity of the “magnetic” nodes are yet small.

In the range of parameters where significant aggregation occurs ( $\lambda > 7.0$ ) the volume defect changes faster but the saturation levels are attained at much larger values of the magnetodipolar parameter than in the case of an MFG with  $\sigma = 0$ .

Notably, at large NP concentrations for all the studied values of  $\lambda$ , the volume defect changes non-monotonically: its magnitude displays maximum about  $c = 0.65$ . In our view, for the weaker dipoles (say,  $\lambda \leq 7$ ) such a feature is result of mutual competition of dipolar forces of closely positioned particles, i.e., the self-averaging of the local fields combined with lower compliance of anisotropic NPs to those forces. Under strong dipole interaction, the most probable reason of  $\Delta V$  decrease is formation of rather extended NP chains which go through the whole sample thus making it less dense.



**Figure 5.** (Colour online) Volume defect of an MFG sample as a function of concentration  $c$  and magnetodipolar parameter  $\lambda$ : (a) magnetically isotropic particles  $\sigma = 0$  and (b) magnetically anisotropic particles  $\sigma = \infty$ . Solid black lines are isolines of volume, dot-dashed black line renders the average volume between the minimal and the maximal value at the diagram

#### 4. Conclusions

Coarse-grained molecular dynamics simulations are performed of micro-size ferrogel objects with the reference number of magnetic nanoparticles being several hundreds. The structure state of the system might be non-aggregated as well as aggregated (chained) depending on the concentration of the magnetic phase and the intensity of interparticle interaction. With respect to the magnetodipolar parameter, the structure changes might be treated as a transition which is quite sharp for the microferrogels comprising magnetically soft particles and rather smeared for those comprising magnetically hard ones. The samples with the particles of different anisotropies possess substantially different magnitudes of the volume defect, i.e., effective density, as well. The results obtained show that the simulated MFGs can be used, in principle, to study the locking ability of microferrogels to carry microscale cargo since, under a fixed amount of incorporated particles, this ability depends on the structure of spontaneous configurations of the sample.

#### Acknowledgments

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