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Low temperature structural transitions in dipolar hard spheres: The influence on magnetic properties

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ABSTRACT

We investigate the structural chain-to-ring transition at low temperature in a gas of dipolar hard spheres (DHS). Due to the weakening of entropic contribution, ring formation becomes noticeable when the effective dipole–dipole magnetic interaction increases. It results in the redistribution of particles from usually observed flexible chains into flexible rings. The concentration (ρ) of DHS plays a crucial part in this transition: at a very low ρ only chains and rings are observed, whereas even a slight increase of the volume fraction leads to the formation of branched or defect structures. As a result, the fraction of DHS aggregated in defect-free rings turns out to be a non-monotonic function of ρ. The average ring size is found to be a slower increasing function of ρ when compared to that of chains. Both theory and computer simulations confirm the dramatic influence of the ring formation on the ρ-dependence of the initial magnetic susceptibility (χ) when the temperature decreases. The rings due to their zero total dipole moment are irresponsive to a weak magnetic field and drive to the strong decrease of the initial magnetic susceptibility.

1. Introduction

Nowadays magnetic soft materials form an emerging area of soft matter research, as they provide a possibility to efficiently control their behaviour by an external magnetic field. A lot of promising applications of magnetic soft materials in medicine, robotics and industry [1–9] rely on the detailed understanding of the relationship between the nano-scale structure of these materials and their microscopic responses. Magnetic nanoparticles tend to form various structures due to the anisotropic interparticle dipole–dipole interaction. In order to focus on the magnetic interactions and get rid of often non-crucial steric (chemical) details of the interactions, theoreticians and computer scientists usually employ the model of DHSs to investigate and predict structural and phase transitions in dipolar soft matter.

One of the well-known and actively studied examples of dipolar soft matter is magnetic fluids (ferrofluids). Synthesised in the 1960s [10], these systems are suspensions of magnetic single-domain nanoparticles in magnetopassive carriers. Ferrofluids prove to have a complex microstructure. Chain aggregates composed by magnetic particles are responsible for magnetooptical [11–13], rheological [14–16], scattering [17–20] and many other anomalies usually observed in magnetic fluids when an external field is applied. As such, ferroparticle chains became a subject of numerous theoretical [21–26] and simulation [27–40] studies. The main conclusion of these works is that the chains are very flexible, and their average length, as well as the concentration, rapidly grow with decreasing temperatures and increasing concentration. In addition, ferroparticle chains, being highly correlated objects, inevitably contribute to a sharp increase of the initial magnetic susceptibility [26].

Lately, the investigation of DHS at low temperatures revealed the existence of a different cluster type, namely ferroparticle rings [28,41–43,37,38]. Their formation is to be expected, as the long flexible chains close the magnetic flux when collapsing into rings. Despite the loss of entropy, a ferroparticle ring is energetically more advantageous, that is why the ideal ring of DHS was proven to be a ground state in quasi 2D [44]. Unlike chains, ferroparticle rings have a very weak response to an applied magnetic field, and do not contribute to the increase of χ [45]. In Ref. [40] the structural transition at low temperature, earlier obtained in simulations, was accurately quantified theoretically and was shown to be directly responsible for the nonmonotonic temperature dependence of the DHS gas initial magnetic susceptibility. However, in the work [40] only very low concentrations were

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addressed to guarantee that all clusters were well defined rings and chains, and the intercluster interactions, as well as the deviations of cluster topologies from the "ideal" ones, were irrelevant. In the present contribution we continue scrutinising the structural peculiarities of the DHS gas at low temperatures, but for much broader range of particle concentrations. As such, the present study allows to find the concentration dependence of cluster topology and to clarify the limitations of the previously developed approach [40]. For the first time (to our knowledge), we pinpoint the concentrations at which the branched structures start emerging.

The paper is organised as follows. In Section 2 we discuss Monte Carlo simulation results and theoretical predictions on the chain and ring concentrations and their average sizes. Here, we show that the non-monotonic ρ-dependence of the fraction of DHSs aggregated in defect-free rings is a signature of a more complex structure forming already at very low concentrations. One of the possible structures, suggested in Ref. [46], is a "Y"-shaped structure obtained via amalgamation of three chains. Recently, we systemised defect structures in Ref. [47], where we showed the importance of branched rings as well. Our detailed investigation of ring structures provided in this section brings out the concentration range in which the "ideal" structures start being replaced by more sophisticated topologies. In Section 3 we show two distinct temperature regimes for the ρ-dependence of χ. At rather high and intermediate temperatures, where the majority of particles either remain non-aggregated, or become members of chains, χ monotonically increases with concentration and inverse temperature. In contrast, for low temperatures, at which rings start dominating in the system, χ increases with concentration, but decreases with inverse temperature. The summary and a short outlook are provided in the Conclusion.

2. Chain-to-ring transition

To investigate the structural transition in DHS gas, we use a combination of Monte Carlo simulations and Density Functional Theory.

Monte Carlo simulations are performed in the canonical ensemble of $N=5000$ particles. Implementing the advanced volume-bias techniques [48,37] allows us to equilibrate the systems at rather low temperatures. Metallic periodic boundary conditions in combination with Ewald summation are used. In simulations the following criterion was applied: two particles are considered as bonded if their interaction energy is negative and if their relative distance is smaller than 1.3 of particle diameter [38]. For further details on the simulation approach, see Ref. [37]. Here, we distinguish between three types of clusters, namely chains, rings and branched structures. Branched structures are composed by chains and rings connected to each other via the so-called "defects" (particles that have more than two bonded neighbours) [47], which is why chains and rings will be addressed as defect-free clusters in the present paper.

In theory, instead, only defect-free clusters are taken into account. The free energy (F) of a DHS gas can be written as a functional of n-particle chain (g_n) and ring (f_n) volume fractions [49–52]:

$$\frac{F[\{g_n\},\{f_n\}]}{VkBT} = \sum_{n=1}^{\infty} g_n \ln\frac{g_n v}{eQ_n} + \sum_{n=5}^{\infty} f_n \ln\frac{f_n v}{eW_n}, \quad (1)$$

where V stands for the system volume, k_{BT} is the thermal energy, v has a meaning of the particle volume. Q_n and W_n denote the chain and ring partition functions respectively, whose calculations have been performed in Ref. [40]. Following the results of Ref. [44] and numerical results [53,37,38], we assume that rings smaller than five particles do not form. In our calculations we assume chains to be flexible and rings to have an ideal circular shape.

The minimisation of the free-energy functional (Eq. (1)) with respect to the distributions $\{g_n\}$ and $\{f_n\}$ preserving the concentration $\rho = 6Nv/\pi V$:

$$\sum_{n=1}^{\infty} g_n n + \sum_{n=5}^{\infty} f_n n = \frac{\pi}{6}\frac{\rho}{v}, \quad (2)$$

leads to the following solution:

$$g_n = \frac{1}{v} Q_n p^n, \quad f_n = \frac{1}{v} W_n p^n. \quad (3)$$

Here, p, the Lagrange multiplier to be found from Eq. (2), has the meaning of activity.

In the present paper we use the dimensionless temperature $T_* = 6vk_BT/\pi m^2$, where m is the particle magnetic moment. This temperature is the inverse dipolar coupling parameter, characterising the energy per particle of two touching DHS with coaligned dipolar moments in units of k_BT.

We start describing the low-T^* behaviour of DHS gas by plotting the distributions of defect-free chains and rings over their sizes. In this case, it is convenient to use normalised fractions of n-particle clusters:

$$C_n = \frac{6}{\pi}\frac{nvg_n}{\rho}, \quad R_n = \frac{6}{\pi}\frac{nvf_n}{\rho}. \quad (4)$$

These functions show the fraction of particles belonging to a corresponding cluster of a fixed length. The fraction of single particles is given by C_1. Note that for R_n the value of n is larger than five. In Fig. 1 the characteristic cluster distributions are plotted for $\rho = 5\times10^{-4}$ at various low temperatures. Here, one can see that for the highest $T_* = 0.155$ the majority of particles is aggregated in chains. The amount of particle in rings is rather low. This difference levels out with decreasing temperature, and for the lowest $T_* = 0.125$ we observe an inversion: the population of rings evidently dominates. This crossover shows the presence of a structural transition from the system with mainly chain clusters to that of rings. It is worth mentioning that the position of C_n maximum almost does not depend on T^* and is noticeably closer to unity, than the one for R_n. The latter strongly depends on temperature and shifts towards the larger rings with decreasing T^*. Both distributions become wider on cooling, which is the

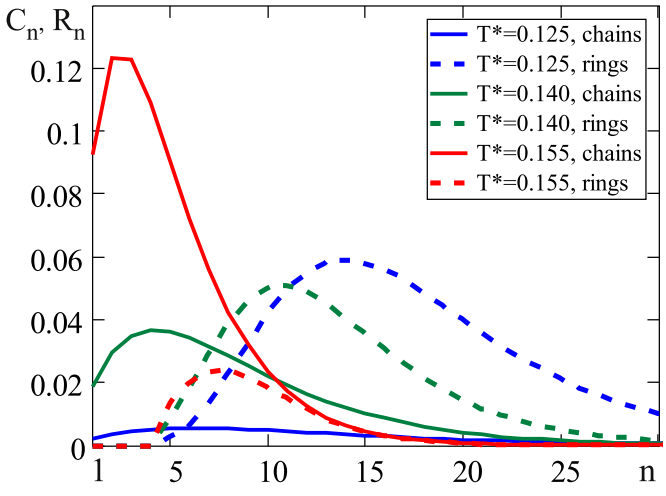

Fig. 1. Distributions C_n and R_n from Eq. (4) at fixed $\rho = 5\times10^{-4}$. Solid lines show the fraction of particles in chains, dashed lines describe those in rings. Dimensionless temperatures are given in the legend. For the sake of clarity we plot here only theoretical predictions that are in a good agreement with the simulation data.

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