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Self-assembly of magnetic nanoparticles into complex superstructures: Spokes and spirals

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Abstract

Dipole–dipole interactions in the most commonly used ferrofluids are relatively weak and there are only a few reports of chain formation in zero magnetic field. Here we report on the pronounced aggregation of a ferrofluid formed by maghemite nanoparticles (10 nm in diameter), investigated by atomic force microscopy (AFM), small angle neutron scattering (SANS) and small angle X-ray scattering (SAXS). The ferrofluid forms chain-like filaments independently of particle concentration. Furthermore, the ferrofluid forms self-assembled patterns, namely ordered superstructures, such as spirals, concentric rings and spokes (radially directed lines), when deposited on a substrate under a magnetic field. Our results reveal an unprecedented level of complexity in the self-assembly of magnetic nanoparticles. Further optimization of the working conditions could eventually enable the reproducible creation of three-dimensional magnetic structures with chosen architecture on submicron length scales.

Keywords: Magnetic nanoparticles; Ferrofluids; Micro-patterns; Self-assembly; AFM

1. Introduction

Ferrofluids are colloidal fluids composed of solid, single-domain magnetic particles, of diameter between ca. 3 and 15 nm, normally coated with a surfactant shell or possessing a charged surface, suspended in a liquid carrier. In surfactant-stabilized ferrofluids the steric hindrance of the surfactant molecules normally counteracts the dipole–dipole attraction between the magnetic moments of the particles and the isotropic van der Waals attraction between the magnetic cores, so that the suspensions are stable [1]. However, under an applied magnetic field some ferrofluids form chain-like aggregates in which the dipoles are oriented in a head–tail configuration along the direction of the field [2,3]. These chains can further aggregate and form bigger columnar aggregates. Several experimental, theoretical and simulation studies have tried to explain the occurrence of a spatial modulation in the particle density and the formation of aggregates under applied magnetic fields, but this process is still not completely understood [4–10]. Furthermore, theoretical predictions [2,3] and molecular dynamics simulations of dipolar fluids have proposed that chain-like structures can be formed also in absence of a magnetic field [11–13], and so far a few cases of chain-like aggregation have been experimentally observed [14–17]. Since dipole–dipole interactions increase quadratically with the particle volume, it is expected that only larger particles may form chain-like and ring-like aggregates. Indeed the smallest particles so far reported to form chains are about 15 nm in diameter [15].

Due to their magnetic characteristics, ferrofluids have been successfully employed in a variety of technological applications, from sealing to ink-jet printing [18]. Recently interest in ferrofluids has been revived by the potential application of patterned arrays of discrete single-domain nanoparticles in high density storage [19] and optical devices [20].

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Many techniques have been proposed to assemble nanometric building blocks into mesoscopic arrays, either in periodically ordered superlattices [21–24] or in patterns with controlled geometry. The latter require a pre-patterning of the substrate (for example by micro-contact printing [25]) and subsequent surface decoration [26]. The existing techniques require a long and expensive preparation, and are restricted to a few achievable structural motives, such as chains [27], rods and superlattices [28,29] or spheres [30].

Our experiments show that in the absence of a magnetic field a suspension of very small maghemite nanoparticles (10 nm in diameter) forms small aggregates, often of chain-like structure. Most importantly, upon evaporation of the solvent on a solid substrate and under a weak magnetic field, the suspension of maghemite nanoparticles forms complex-ordered patterns, such as spokes, spirals and concentric rings. To our knowledge this is the first time that such structures have been observed and imaged at high resolution. The great variety of obtainable structures could potentially lead to new methods of surface patterning.

2. Experimental

Maghemite (γ-Fe_2O_3) nanoparticles were prepared by thermal decomposition of a carbonyl iron complex, $Fe(CO)_5$, in presence of a surfactant, a method which allows fine control of particle size and polydispersity [31]. The maghemite nanoparticles synthesised in this way are coated with oleic acid, and form a stable suspension in cyclohexane, which was characterized by means of small angle neutron scattering (SANS) and small angle X-ray scattering (SAXS). SANS experiments were performed at the V4 instrument at BENSC (Hahn–Meitner Institute, Berlin). A magnetic field of 1 T was applied to the sample, in a direction perpendicular to the incoming neutron beam. SAXS measurements were performed by means of a Kratky small angle X-ray camera (Hecus X-ray Systems GmbH, Graz, Austria), equipped with a Rich Seifert & Co. X-ray tube (Iso-Debyeflex 3003) and a position sensitive detector (PSD-50M, M. Braun). These measurements were performed in absence of an applied magnetic field. The smearing effect due to the slit length was eliminated from SAXS curves using the method of Singh et al. [32].

For the microscopic investigation, the suspension of maghemite nanoparticles (concentration 8.7×10^{-4} M, volume fraction $\phi = 2.8 \times 10^{-5}$) was deposited on a thin freshly-cleaved (atomically smooth) mica substrate and the cyclohexane was allowed to evaporate at room temperature. The resulting film of nanoparticles on the substrate was then imaged by atomic force microscopy (AFM; Explorer 2000 Topometrix, Santa Barbara, USA). To study the effect of an applied magnetic field, the mica surface was placed directly on top of a $Nd_2Fe_{14}B$ permanent magnet (Vacodym 745HR, Vacuumschmelze, Hanau, Germany; maximum field ca. 1.44 T) during the deposition of the suspension and evaporation of the solvent. The average distance of the deposited film to the underlying magnet is approximately equal to the mica thickness, i.e. a few hundred micrometers. The surface roughness of the magnet is negligible because the magnet is polished by the manufacturer. We also repeated the experiments under a magnetic field parallel to the substrate created by an electromagnet normally used for ESR experiments (Bruker Biospin; power supply ER081, maximum field ca. 1 T). In this case the sample was placed between the two coils of the magnet, a few centimetres away from the designated ESR capillary holder.

3. Results

SANS and SAXS spectra of the ferrofluid, shown in Fig. 1 were analysed by dividing the spectra in two regions, based on the values of the scattering vector Q. The region at higher Q values establishes the size and size distribution of the particles, whilst the region at low Q values contains information about the presence and type of aggregates. The SANS and SAXS results in the high Q region were fitted simultaneously according to a core-shell model (polydisperse spherical cores surrounded by a shell of uniform thickness) [33]. In particular, the same values of physical parameters such as particle shape, size and polydispersity, and shell thickness were used to best fit both curves; theoretical values of the scattering length densities were used, which are different for neutrons and X-rays. The curve fit (shown in Fig. 1 as solid lines) resulted in a mean radius of 3.5 nm (polydispersity 17%) for the magnetic cores and a uniform oleic acid shell of thickness 1.5 nm. With regards to the low Q region, both curves scale approximately as a power law with exponent −1, which is a clear signature of the presence of cylindrical aggregates

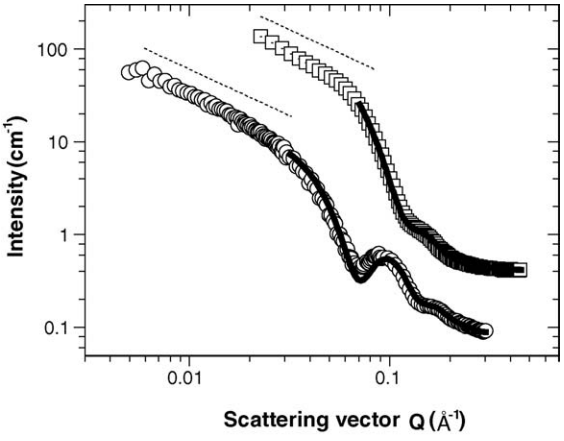

Fig. 1. SANS and SAXS spectra of maghemite suspensions (0.16 M). (Circles) SANS spectrum recorded under an applied magnetic field. (Squares) SAXS spectrum recorded under no applied field. The intensity of these data is in arbitrary units. The error bar is approximately the size of the symbols. Solid lines at higher values of the scattering vector Q represent the best fit of the data according to a core-shell model, from which particle size can be deduced. The dashed lines at lower values of Q are a guide to the eye and indicate $Å^{-1}$ power law (characteristic of chain-like aggregates).