Magnetic Nanorods: Genesis, Self-Organization and Applications

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Magnetic-field-assisted self-assembly of magnetic dipole moment carrying iron nanoparticles is shown to result in the formation of magnetic and mechanically stiff nanoscale rods. The cooperative behavior of an ensemble of such rods and bundles thereof exhibits self-organized pattern formation on different length scales. Pattern formation on large length scales reveals great similarity with physical systems undergoing spinodal decomposition. Possible applications for dipolar magnetic nanorods in the field of perpendicular storage media are highlighted. We discuss an aerosol-synthesis-route allowing to prepare ferrofluids (FF) with shape-anisotropic particles constituting the magnetic phase immersed in the nonmagnetic carrier fluid. These so-called nanorod FF unveil a two orders of magnitude increase of viscosity enforced by an applied field of 10 mT even at shear rates larger than 10^{-2} s. This raises prospects for applications in microfluidics and MEMS.

1. Introduction

Recent progress on magnetism and magnetic materials have made nanostructures a particularly interesting class of materials for both scientific and nanostructured technological explorations. Studies on subjects such as interlayer coupling, giant magnetoresistance, colossal and tunnelling magnetoresistance, exchange bias, half-metallic ferromagnets, spin injection and current-induced switching have eventually led to the exciting possibility of utilizing electron spin for information processing or spintronics [1, 2]. The materials used for either putting the ideas discussed above into practice but also for assembly of prototypical devices merely belong to the class of layered materials-thin film

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and multilayer systems. However, not only nanoscale layered materials manifest fascinating and novel properties, a story of scientific and technological success is evidenced by the large scale application of nanostructured soft and hard magnetic materials [3], which belong to the category of nanostructured bulk materials. Nanoscale particulate composites represent a scenario that covers a broad diversity of materials from biomaterials to superspin glasses, and granular magnetic materials serving as model systems for the study of ageing, rejuvenation and memory phenomena [4]. The fabrication of ordered nanostrutures – essentially utilizing dot-like or rod-like nanometer-sized objects as building units – encompasses a variety of preparation techniques such as different lithography and nanoimprint techniques, copolymer nanolithography, as well as self-assembled and nanotemplate-assisted growth of nanostructures [5].

Fundamentally, novel and unexpected physical effects will emerge when the sample size and/or some characteristic length scale of microstructure becomes comparable or even smaller than a property-dependent characteristic length scale such as the carrier mean free path, various magnetic exchange lengths, or the spin diffusion length [6]. This rationale has been the driving force for the development of increasingly sophisticated materials, as discussed above. Dimensional analysis of the well-known micromagnetic free energy yields two fundamental length scales. The wall-width parameter $\delta_0 = (A/K)^{1/2}$ (A being the exchange stiffness, and K the magnetocrystalline anisotropy) that is varying from a few nm in extremely hard materials to more than 100 nm in very soft materials. It determines the thickness of magnetic domain walls and the spatial response of the magnetization to local perturbations. Secondly, the exchange length $l_{\text{ex}} = \sqrt{A/(\mu_0 M_s^2)}$ (M_s : saturation magnetization) which describes the competition between interatomic exchange and magnetostatic self-interactions; experimentally found exchange lengths are on the order of 10 nm [7]. There are other relevant length scales such as the critical single-domain size [6] $R_{\rm SD} = 36\sqrt{AK}/(\mu_0 M_s^2)$ of a sphere $(R_{\rm SD}({\rm Fe}) \cong 6 \,{\rm nm})$ $R_{\rm SD}({\rm Co}) \cong 34 \,\mathrm{nm}, R_{\rm SD}({\rm SmCo}_5) \cong 764 \,\mathrm{nm})$ and domain sizes specifying the real space scale above which inhomogeneous magnetization states extend throughout the material. In magnets with random magnetic anisotropy, the magnetic correlation length $L \propto D^{-3}$ yields a measure of how many grains of size D exhibit strong intergranular correlations [8]. A length scale, particularly relevant to storage media, specifying the size below which the material appears no longer ferromagnetic is the superparamagnetic limit characterized by $KV \approx k_{\rm B}T$, where V denotes the particle volume; we note that the observation of superparamagnetic behaviour depends on the time frame of measurement. In the superparamagnetic state, thermal fluctuations are sufficiently strong to overcome an effective energy barrier, basically set by the magnetocrystallineand shape anisotropy. Finally, there are two limiting length scales in magnetism, the Fermi wavelength reflecting intra-atomic electrostatic interactions, and the correlation length describing the physical behaviour near critical points e.g. at the ferro- to paramagnetic phase transition [6].

A recent upsurge in research on magnetic nanostructures puts much emphasis on understanding of ordered arrangements or patterned arrays of building units which are confined in two (rod-like) or three dimensions (dot-like) [5]. Advanced sample growth and patterning techniques allows one to control and modify shape and size of building blocks and likewise the geometry of patterned arrays of such entities. As a result, highly ordered arrangements of magnetic building units serve now as candidate systems for studying and understanding mesoscopic effects generated by the simultaneous manifestation of geometric confinement, physical proximity and presence of structural order. Altogether, they govern the interplay between the relevant physical length scales (as discussed above) and the scales and measures related to size, shape and degrees of imperfections of the building blocks as well as the geometry/topology of their spatial arrangements.

In studying arrays of nanometer-sized building units, it has been found that in particular *proximity* in many cases interferes with the physical length scale associated with long-ranged interaction phenomena, in this context represented by the dipolar interaction which decays $\propto 1/r^3$. In a simplistic approach, assuming building blocks which have single domain character and therefore may be approximated by magnetic dipoles, the dipolar field generated by an individual building unit and its interaction with nearest neighbor dipoles may yield a rather intuitive picture of the magnetic configuration and some of the properties of the overall array. However, whenever the distance between the building units becomes comparable to their size, the simple dipolar approach fails. A more realistic estimate of the effects of dipolar fields in arrays of nanostructures requires a minimization of the magnetostatic self-energy, which in turn vields the stable magnetic configuration of the array. This is a formidable task, since the local values of the magnetization $M(\mathbf{r})$ and the local demagnetizing field $\mathbf{H}_{d}(\mathbf{r})$ are to be integrated over all sample volume. Nevertheless, many new phenomena have been discovered and are essentially related to proximity effects in patterned arrays of nanostructures, such as enhancement or decrease of coercivity, changes of the switching field width, shape- and interactioninduced anisotropies as well as shifts of the spin-wave excitation frequencies to name just the most prominent effects [5].

In summary, it seems fair to conclude that the dipolar interaction manifests a constitutive force in determining and controlling the properties of ordered arrays of nanostructures, artificially grown or prepared by utilizing *e.g.* lithography-, nanoimprinting- or template-assisted growth techniques. In what follows, we are going to discuss a complementary phenomenon focussing on the *self-organized* pattern formation of magnetic nanoparticles which serve as building units. Again, the dipolar interaction has been identified as the force of creation, thus controlling and dominating the morphogenesis. As discussed above, we will treat the individual nanoparticles in a simplistic manner as magnetic dipoles. In chapter two, their single-particle behavior is discussed in terms of the Stoner–Wohlfahrt model, moreover, the limiting cases of two interacting dipoles and an ensemble of otherwise unconfined dipoles are addressed. Chapter three deals with the understanding and modelling of the evolution of regular patterns observed during morphogenesis. Potential ramifications to nanofabrication in the area of high-density perpendicular storage media are highlighted. In chapter four, we discuss how the magnetoviscous properties of ferrofluids can be enhanced by tailoring the shape-anisotropy of the magnetic phase dispersed in a nonmagnetic carrier fluid.

2. Magnetic properties of nanoparticles

2.1 The Stoner–Wohlfarth model

The Stoner–Wohlfarth (SW) model [9] is one of the simplest approaches for describing hysteresis effects in magnetism. It can be used to describe the magnetization curve of a collection of noninteracting identical single domain particles. In the simplest case, the magnetic energy E of an individual particle has contributions from uniaxial magnetic anisotropy and from the interaction of the particles' magnetization vector **M** with an applied magnetic field **H**,

$$E = KV\sin^2\theta - \mu_0 V\mathbf{H} \cdot \mathbf{M} \,. \tag{1}$$

Here, *K* denotes the effective uniaxial anisotropy constant, *V* is the volume of the particle, θ represents the angle between the anisotropy axis and **M**, and μ_0 is the permeability of free space. Within the SW model, the particles are assumed to be sufficiently small so that strong exchange forces hold all the atomic spins parallel and, consequently, any space dependence of the magnetization can be neglected. On the other hand, the particles should be large enough to avoid temperature effects (see below).

For given materials parameters and for a given orientation of the anisotropy axis with respect to the applied field, the magnetization curve of a single particle can be obtained by minimizing Eq. (1) with respect to the angle between **M** and **H**. When the uniaxial anisotropy axis is parallel to **H**, the hysteresis loop has the well-known rectangular shape, with a remanence M_r which is equal to the saturation magnetization M_s and with a coercivity (switching field) $H_c^0 = 2 K/(\mu_0 M_s)$. On the other hand, no hysteretic behavior results for a perpendicular orientation between the anisotropy axis and **H**. For a sample of randomly oriented noninteracting uniaxial particles, $M_r = \frac{1}{2} M_s$ and $H_c \cong 0.479 H_c^0$ [9].

2.2 Magnetic anisotropy

The origin of the assumed uniaxial magnetic anisotropy in Eq. (1) may be due to the dipole–dipole interaction (shape anisotropy) and/or due to the combined effect of the crystal-field and spin–orbit interaction (magnetocrystalline anisotropy). Other types of anisotropy which may be of relevance in the context of nanoparticle magnetism such as surface anisotropy or exchange anisotropy will be ignored in the following discussion. The general expression for the magnetostatic shape-anisotropy term $E_{\rm M}$ of a homogeneously magnetized ellipsoid is [10]

$$E_{\rm M} = \frac{1}{2} \mu_0 V \left(N_x M_x^2 + N_y M_y^2 + N_z M_z^2 \right), \qquad (2)$$

where N_x , N_y , and N_z denote the demagnetizing factors along the principal (*e.g.*, Cartesian) axes of the ellipsoid, and M_x , M_y , and M_z are the respective Cartesian components of the magnetization. For the particular case of an elongated cigar-shaped prolate spheroid (with two equal axes), Eq. (2) simplifies to

$$E_{\rm M} = \frac{1}{2} \mu_0 V(N_x - N_z) M_{\rm s}^2 \sin^2 \theta + \text{const.}, \qquad (3)$$

where we have assumed $N_x = N_y$ and $M_z = M_s \cos \theta$. Equation (3) reveals the same functional form as the first term on the right hand side of Eq. (1), with the effective shape-anisotropy constant $K = K_s = \frac{1}{2} \mu_0 (N_x - N_z) M_s^2$.

The magnetocrystalline anisotropy energy E_k expresses the dependency of the magnetic energy of a particle on the orientation of its magnetization **M** relative to the crystal axes. For a particle with uniaxial magnetocrystalline anisotropy, E_k is generally expanded in terms of the angle θ between **M** and the anisotropy axis, which is *e.g.* the *c*-axis in hcp Co,

$$E_K = K_1 V \sin^2 \theta + K_2 V \sin^4 \theta + \dots , \qquad (4)$$

where K_1 and K_2 are functions of temperature. The use of cubic magnetocrystalline anisotropy in Eq. (1) instead of or in addition to uniaxial anisotropy as well as the incorporation of higher-order (K_2) terms is straightforward.

It is of interest to compare the magnitude of magnetocrystalline anisotropy with the strength of shape anisotropy. At room temperature, the magnetocrystalline anisotropy constants of single crystals of Ni, Fe, and Co are, respectively, $-5.7 \times 10^3 \text{ J/m}^3$, $4.7 \times 10^4 \text{ J/m}^3$, and $4.5 \times 10^5 \text{ J/m}^3$ [11]. By using the saturation-magnetization values $M_s(\text{Ni}) = 500 \text{ kA/m}$, $M_s(\text{Fe}) = 1700 \text{ kA/m}$, and $M_s(\text{Co}) = 1400 \text{ kA/m}$, we see that for an elongated particle (with $N_x = 1/2$ and $N_z = 0$), the corresponding values for the shape-anisotropy constants, $7.9 \times 10^4 \text{ J/m}^3$, $9.1 \times 10^5 \text{ J/m}^3$, and $6.2 \times 10^5 \text{ J/m}^3$, are (at least for Ni and Fe) much larger than their magnetocrystalline counterparts.

2.3 Pole avoidance

The dipole-dipole interaction is usually the most complicated energy term, since it requires evaluating the interaction of each atomic magnetic moment



Fig. 1. Bright-field TEM image of an ensemble of Fe nanoparticles. The pole avoidance principle supports the formation of flux-closure patterns (ring structures).

with the magnetic field which is created by all the other dipoles. The complexity of the problem can easily be grasped by considering the well-known textbook case of two isolated dipoles. Equation (5) describes the mutual interaction energy $E_{1,2}$ between two magnetic moments \mathbf{m}_1 and \mathbf{m}_2 separated by a distance $\mathbf{r}_{1,2}$ ($r_{1,2} = |\mathbf{r}_{1,2}|$),

$$E_{1,2} = \frac{\mu_0}{4\pi} \left[\frac{\mathbf{m}_1 \cdot \mathbf{m}_2}{r_{1,2}^3} - \frac{3 \left(\mathbf{m}_1 \cdot \mathbf{r}_{1,2} \right) \left(\mathbf{m}_{1,2} \cdot \mathbf{r}_{1,2} \right)}{r_{1,2}^5} \right].$$
(5)

When the dipoles are forced to align in parallel with the moment direction along the separation distance, then the parallel "head-to-tail" configuration is the one with the lowest energy. On the other hand, when the collinear dipoles are constrained to have their moments oriented perpendicularly to the separation distance, antiparallel alignment is energetically favoured. This relatively simple example suggests that in realistic experimental situations, where usually a large number of particles, wires, *etc.* are involved, the problem of finding the ground state of the magnetostatic energy is rather complicated, and it is difficult to predict whether the effect of the dipolar interaction is *e.g.* to prefer parallel or antiparallel alignment of magnetic moments.

Nevertheless, based on the energetics, some general statements on the qualitative behaviour of a large number of building blocks can be made [10]. The magnetostatic energy is positive definite, $E_{\rm M} \ge 0$, and prefers magnetization structures with no so-called surface and volume poles, *i.e.*, configurations where both terms $\mathbf{n} \cdot \mathbf{M}$ (surface charges) and $-\nabla \cdot \mathbf{M}$ (volume charges) vanish; here, \mathbf{n} denotes a unit vector which is normal to the surface of the magnetic specimen. The above statement is known as the pole-avoidance principle. The most prominent manisfestation of this rationale is the formation of so-called flux-closure patterns which are characterized by the tendency to min-

imize $E_{\rm M}$. As an example, Fig. 1 shows the realization of pole avoidance on the nanoscale: eventually, a chain of sufficiently large nanoparticles will bend and form a closed ring structure, once the number of particles reaches a certain critical value.

2.4 Magnetic relaxation

As indicated in Sect. 1, the SW model is valid only at zero temperature. At nonzero temperatures, the thermal energy $k_{\rm B}T$, where $k_{\rm B}$ denotes the Boltzmann constant, may induce transitions between local energy minima. When the associated relaxation time is comparable to the characteristic time of the measurement, which in the case of dc magnetization is typically a few seconds, time-dependent effects become important, since the magnetic properties change during measurement.

Within the Néel–Brown theory of superparamagnetism, the magnetic relaxation time τ_N of a particle exhibiting uniaxial magnetic anisotropy is given by [10]

$$\tau_{\rm N} = \tau_0 \exp\left(\frac{KV}{k_{\rm B}T}\right) \,, \tag{6}$$

where $\tau_0 \cong 10^{-9} - 10^{-10}$ s, and *KV* denotes the anisotropy-energy barrier. At zero applied magnetic field, Eq. (6) describes the average time it takes for the magnetic moment to jump between the two equivalent energy minima at $\theta = 0$ and $\theta = \pi$ (compare Eq. (1)).

When the particles are dispersed in a fluid of viscosity η , an additional relaxation mechanism, the so-called Brownian rotational-diffusion mechanism comes into play. Brownian relaxation is characterized by a switching time

$$\tau_{\rm B} = \frac{3 \, V_{\rm H} \, \eta}{k_{\rm B} \, T} \,, \tag{7}$$

where $V_{\rm H}$ denotes the hydrodynamic volume of a single particle. In general, both mechanisms Néel and Brown relaxation take place, resulting in an effective relaxation time [12]

$$\tau_{\rm eff} = \frac{\tau_{\rm N} \, \tau_{\rm B}}{\tau_{\rm N} + \tau_{\rm B}} \,. \tag{8}$$

3. Self-organized pattern formation of magnetic nanoparticles

3.1 Self-organization

Ordinary states of matter like a layer of fluid, a mixture of chemicals, granular or genetic material can exhibit under appropriate conditions a multitude of self-organization phenomena on a macroscopic scale in the form of spatial patterns, temporal rhythms or spatiotemporal order [13]. We may regard such patterns as global emergent properties of the system, since the scale of ordering vastly exceeds the range of interactions of the constituents, and there is no obvious hint of a length scale of this magnitude in the microscopic physics of the unpatterned state. In its essence, the understanding of pattern formation relies on the concept of instabilities of a reference state [14, 15]. In experiment, such instabilities arise when a system in equilibrium is driven into non-equilibrium states by increasing an externally manipulable control parameter. Along its path the dynamical system eventually becomes infinitely sensitive to fluctuations (perturbations) and responds by growing disturbances - the onset of symmetry breaking - in a spatially uniform state [16]. The crucial next step in the pattern-forming process rests on some built-in nonlinear mechanisms that enable the driven away-from-equilibrium system to create and sustain new states of matter, displaying regulatory behavior in space and/or time which would be exceedingly improbable to occur under equilibrium conditions [14, 17]. Non-equilibrium spontaneous pattern formation implies that the constituents of the system must be able to communicate via an extraordinary manner of cooperativity over distances much longer than those to which they are accustomed at equilibrium.

3.2 Experimental

We study magnetic-field-assisted self-assembly of magnetic dipole moment carrying aerosol-grown iron nanoparticles in an aerosol flow condenser. The precursor iron pentacarbonyle is evaporated at a rate of 1 µl/min into a continuous flow of 500 standard cubic centimeter per minute (SCCM) of inert gas argon at a pressure of 15 mbar and thermally dissociated in a furnace held at 950 °C. The released iron atoms grow by condensation and coagulation and finally form magnetic nanoparticles. Further downstream they are collected on a liquid nitrogen cooled flat substrate in the presence of a homogeneous magnetic field of 0.2 T, oriented perpendicular to the substrate plane; the details of the preparation are discussed in [18]. Enforced by the dipolar interaction, the early stage of particle collection is dominated by a head-to-tail arrangement of individual particles. Assisted by the external field, the system further evolves by forming arrays of string-like objects. The homogeneous field is applied to prevent the system from taking a path into a magnetically disordered (frustrated) state, which is difficult or even impossible to analyze. The task of the applied external field is twofold: first, it aligns the particles moment head-to-tail perpendicular to the substrate plane, and secondly, the flux of the overall field becomes concentrated along the already deposited particles resulting in localized field gradients which exert attractive forces on arriving particles thereby guiding them to the head-ends of the already deposited particles. This process is self-sustaining and strongly favors parallel arrangement of individual dipoles and, likewise, supports the formation of string-like particle chains. Therefore, what actually remains to be studied and understood is the collective behavior of such string-like magnetic moment carrying objects in the presence of a homogenous *i.e.* no force exerting magnetic field of variable strength.

Evidence for the formation of particle chain segments, driven by dipolar interaction, has been found in ferrofluids (dispersions of magnetic colloids) even in zero magnetic field [19]. When applying an external field, the dipolar character of the linear chain segments leads to their alignment along the field direction and a concomitant transition from individual chains to large aggregates of chains. Chain-chain interaction between nearly parallel rod-like dipolar objects has been proposed to result in attraction between parallel oriented chains [20]. However, the experimental study of chain-chain interaction in dipolar fluids is hampered by the fact that particle chains are fluctuating objects that thermally dissociate (chains "melt" with increasing temperature) and again recombine to chains with decreasing temperature [21]. Moreover, the spatial and orientational correlations of individual chains crucially depend on the magnetic coupling between individual particles [22], which is strongly influenced by surfactants covering the particles' surfaces. As a result, it seems that a necessary prerequisite for studying and understanding the collective behavior of one-dimensional dipolar objects is solid-like rigidity between neighboring particles, so that string-like objects can be treated as mechanically stiff magnetic rods.

In the following, we are going to demonstrate that aerosol-grown magnetic iron nanoparticles when deposited on a substrate in the presence of a homogeneous magnetic field form an array of dipolar rigid rods. It is the reduction of the particles' free surface energy that yields the driving force for neck formation (sintering) [23] between neighboring particles, thus favoring the emergence of solid magnetic rod-like entities. With increasing particle supply, the rod length increases, bundles of rods appear, and eventually the system undergoes a hierarchy of structural instabilities to form self-organized patterns. A schematic of successive stages of morphogenesis is shown in Fig. 2. The experimentally observed structures and patterns are displayed in Fig. 3. Obviously, self-assembled structures occur on all length scales starting at the nanometer scale but also covering the micrometer regime. We consider the hexagonal pore carpet as the most prominent feature of pattern formation and, therefore, we direct our focus on understanding the emergence of pore pattern in the following paragraphs.

3.3 Pattern formation: modelling and discussion

In order to rationalize the process of pore formation, we assume bundle density fluctuations to appear in the homogeneous bundle carpet by laterally bending of individual bundles. At short bundle lengths, the solid-like rigidity of individ-



Fig. 2. Schematic representation of the evolution of form and patterns during magnetic field assisted deposition of iron nanoparticles on a non-magnetic substrate. (a) The particles' magnetic moment (white arrows) becomes aligned parallel to the external field H_0 during deposition. (b) Magnetic field assisted self-assembly of individual dipolar rods (for more details see Sect. 3.3). The build-up of field gradients is symbolized by flux-lines. (c) Further growth of individual rods is accompanied by a change in growth mode resulting in the formation of bundles of rods. Each bundle having a typical diameter of 1 µm constitutes a network of a few hundred rods. The center-to-center distance d_0 between nearest neighbor bundles is about 5 µm. (d) The system of bundles carrying the magnetic flux gives now the appearance of a carpet with homogeneous bundle density $n_0 \propto 1/d_0^2$, and bundle length ℓ . The consequences of bundle-bundle interactions are summarized in (e). (e) When the carpet grows beyond a critical length of $\ell_c \approx 40 \,\mu$ m, the bundles start bending so that funnel-like pores of zero-bundle-density with a typical distance of $\lambda_c \approx 300 \,\mu$ m develop. Since the number of bundles is conserved, pore formation is associated with an enhancement of bundle density in the space around pores.

ual bundles gives rise to an elastic restoring force, which limits the amplitude of fluctuations to infinitesimally small values. With increasing bundle length ℓ , the system of homogeneous bundle density is driven into non-equilibrium and becomes sensitive to infinitesimal density fluctuations. Eventually, symmetry becomes broken by spontaneously developing pores. It appears that individual pores emerge by tilting bundles radially outward relative to the pore-center axis thereby generating bundle density gradients in the space between pores. We describe the geometry of a pore by introducing the tilt angle $a(\mathbf{r}, t)$ that measures the obliquity of bundles relative to its pore-center axis. The lateral arrangement of pores across the substrate exhibits hexagonal symmetry implying that the relevant constituents of the system must be able to communicate in a highly cooperative manner over distances which are comparable to the system size of tens of millimeters.

The fundamental observation, also manifesting a mode of collective behavior, concerns the tilt angle *a*: tilt angles of individual pore forming bundles



Fig. 3. Pattern formation in a 40 μ m thick layer of iron aerosol particles deposited in a homogeneous magnetic field. (a) TEM bright-field micrograph of an isolated Fe-particle chain, obtained by ultrasonic disintegration of a Fe-chain bundle. (b) TEM bright-field micrograph of a single Fe-chain bundle, grown on a TEM grid at a low deposition rate, illustrating entanglement of individual particle chains at large ℓ . (c) Top-view SEM micrograph of a 40 μ m thick layer of Fe-chain bundles manifesting self-organized density modulations in the form of blossom-like pores arranged in a pattern exhibiting (local) hexagonal symmetry. The core regions of edge dislocations in the ordered arrangement of pores are marked by circles. (d) Magnified single blossom-like pore of (c). All SEM and TEM viewgraphs were taken *ex situ*. Exposure of the as prepared structures and patterns to ambient atmosphere resulted in thin oxide layer protecting the Fe-core structures [24].

cancel out when averaged over the total substrate area A so causing $\langle a \rangle_A = 0$. In other words, the tilt angle is a globally conserved quantity and, therefore, must satisfy a continuity equation

$$\langle a \rangle_A = 0 \quad \Rightarrow \quad \frac{\partial}{\partial t} a = -\nabla \cdot \mathbf{J} ,$$
⁽⁹⁾

where \mathbf{J} is interpreted as a tilt-angle current in full analogy to diffusive flux of matter in a system of conserved particle number. In such systems the current is proportional to the local chemical potential gradient and the chemical potential itself is given by the change of free energy density with respect to particle density. Following this guideline, we assume a linear response ansatz for \mathbf{J}

$$\mathbf{J} = -M\nabla\left(\frac{\delta w}{\delta a}\right),\tag{10}$$

Brought to you by | University of Connecticut Authenticated Download Date | 1/11/17 11:02 AM here M describes the mobility of the bundles' top ends when bending occurs, and w is an appropriate energy functional density.

The experimental evidence $\langle a \rangle_A = 0$ together with the fundamental Eqs. (9) and (10) are the basic ingredients we will use to model and understand porepattern formation. Combining Eqs. (9) and (10) yields the nonlinear partial differential equation of the problem $\partial a/\partial t = +M\nabla^2(\delta w[a]/\delta a)$, the solution of which is a formidable task. We prefer simplifying this equation based on assumptions motivated by experimental observations. As we observe bundles being always tilted towards increasing bundle density and never orthogonal to the density gradients, likewise, any chiral character of bundle arrangement is missing, it seems feasible to describe structure formation by a one dimensional approach. Beyond the critical length where the symmetry of the homogeneous system becomes broken, it appears appropriate to orient our coordinate axis to be parallel to the substrate and parallel to the wave vector *k* representing the observed density modulation of the pattern. The remaining task is to construct an expression for the total energy density *w*.

We consider three relevant energy terms entering w. Modelling individual bundles by magnetic dipolar rods, the magnetic dipolar interaction energy density w_m is an obvious contribution to w. Taking only nearest-neighbor interactions into account, w_m is obtained by a Taylor expansion about the homogeneous bundle configuration $a \equiv 0$, and constitutes a nonlinear functional of a(x) and its gradients. The energy associated with bending of bundles with solid-like rigidity is modelled by the bending energy density of a single solid beam, $w_{\rm el}$, multiplied by the local bundle density $n(x) = n_0 + \delta n(x) = n_0 - n_0 \ell (\partial_x a)$ with n_0 being the bundle density of the homogeneous carpet; overall, we obtain $w_{\rm el} \propto a^2/\ell$. Similarly, the interaction energy density $w_{\rm h}$ with the external field H_0 is modelled by that of a single dipole with H_0 multiplied by the local bundle density n(x); $w_{\rm h} = -\mu_0 n(x) m H_0 \cos[a(x)]$ where m is approximated by the saturation magnetization $M_{\rm s}$ of a single rod $(m \propto M_{\rm s} \ell)$. Finally, we obtain for the total energy density

$$w[a(x)] = c_0 + c_2 a^2 + c_4 a^4 + \eta(\partial_x a) + \kappa(\partial_x a)^2 + \cdots,$$
(11)

where $c_0, c_2, c_4, \eta, \kappa$ are coefficients representing the individual energy densities or combinations thereof.

The one dimensional version of the combined Eqs. (9) and (10) inserted with the expression for w reads after linearization

$$\frac{\partial}{\partial t}a(x,t) = (c_2 M) \frac{d^2 a}{dx^2} - (2\kappa M) \frac{d^4 a}{dx^4}.$$
(12)

Equation (12) reflects full analogy to the linearized Cahn–Hilliard equation (C–H eq.) of spinodal decomposition [25–27]. The coefficient

$$c_2 = \frac{ED^4}{40\ell d_0^2} - \frac{3\mu_0 m^2}{d_0^5} + \frac{\mu_0 m H_0}{2d_0^2}$$
(13)

is positive for short rod length, thus, being dominated in the early growth stage by mechanical stiffness of the rods (w_{el}) . However, finally c_2 becomes negative due to the power law increase of the dipolar interaction term $(m^2 \propto \ell^2)$ with increasing bundle length. The coefficient κ remains positive at all length scales. As a result, our analysis clearly identifies ℓ as the external control parameter, and the critical length ℓ_c marking the onset of instability is determined by $c_2(\ell_c) = 0$. The finding that the external field contribution becomes eventually dominated by the dipolar interaction term justifies our notion of magnetic-dipole-interaction-driven spinodal decomposition as a plausible mechanism which triggers spontaneous growth of long-wavelength perturbations in a spatially uniform state. In its essence, the emergence of pores is caused by repulsive dipolar forces; attractive dipolar interactions are effectively suppressed by the missing lateral and horizontal degrees of freedom of movement of individual bundles relative to the substrate plane. Nevertheless, the externally applied field is a necessary prerequisite for pattern formation since, first, H_0 forces the magnetization of the incoming particles to orient parallel to it, and second, the interaction of already deposited particles with H_0 generates the field gradients which stimulate the growth of linear chains and bundles.

We conclude by discussing the central quantitative results obtained from the C–H eq. (12) which is solved by

$$a(x, t) = a_k \exp\{\mathcal{A}(k) t\} \exp(ikx), \qquad (14)$$

with $\mathcal{A}(k) = -M(c_2 k^2 + 2\kappa k^4)$, and k denotes the wave number of a bundledensity-modulation wave. The solution consists of a spatially periodic term and a term describing the time evolution of the amplitude. If $A(k) < 0 \forall k$, all modes k will decay. For $\ell > \ell_c$, modes exist for which $\mathcal{A}(k) > 0$, consequently, the amplitudes grow exponentially. We assume that the fastest growing mode k_c , determined by dA/dk = 0, selects the characteristic length $\lambda_c = 2\pi/k_c$ of the evolving pattern. We find $\lambda_c \approx 1000 \,\mu\text{m}$ and $\ell_c \approx 47 \,\mu\text{m}$ which agree, despite the restrictive assumptions, fairly good with the experimentally found values: $\lambda_c^{ex} \approx 300 \,\mu\text{m}$ and $\ell_c^{ex} \approx 40 \,\mu\text{m}$. Strong evidence for the validity of our simplistic analysis of pore-pattern formation has been obtained by experimentally studying the external field dependence of λ_c . Based on the condition $d\mathcal{A}/dk = 0$, theory predicts $k_c^2 = |c_2|/(4\kappa)$ resulting in $\lambda_c \propto H_0^{-1/2}$ if H_0 is not too small. This power law dependence of λ_c as a function of the externally applied magnetic field H_0 has been reasonably well verified by experiment, see Fig. 4. The observed influence of the field confirms that the pattern formation occurs during deposition and not during removal of the applied field at the end of the deposition process. Finally, we notice that the observed non-equilibrium pore-pattern formation belongs to a subclass of dynamical systems, namely, gradient or potential systems characterized by $\partial a/\partial t = \delta F[a]/\delta a$ [14]. For such sys-

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Fig. 4. Scaling behavior of critical density modulation wavelength λ_c . Normalized average nearest neighbor distance λ_c/ℓ_c of blossom-like pores plotted as a function of the normalized applied magnetic field $\mu_0 H_0/n_0 \Phi$ at fixed bundle length ℓ_c on a log–log-scale (n_0 : homogeneous bundle density; μ_0 : permeability constant; Φ : magnetic flux through a single bundle). The solid line represents a least-squares fit to the data points. From the slope, we determine the power law $\lambda_c \propto H_0^{-0.54\pm0.06}$.

tems the dynamics consists of relaxation towards the minimum in the energy functional F in agreement with the behavior predicted by the C–H equation.

3.4 Possible applications

Apart from pattern formation, magnetic field directed self-assembly may have potential ramifications to nanofabrication, especially in the area of high-density perpendicular magnetic storage media [28–30]. We suggest a manufacturing process that combines lithographically defined generation of ordered structures, which can be created over large areas, with magnetic field directed self-assembly of nanometer-sized static magnetic moment carrying aerosol particles [31]. In fact, our idea relies upon the manufacturing of a lithographically defined master substrate encoding the desired width of and distance between magnetic tracks, as well as enabling to adapt rotationally symmetric arrangement of tracks – the standard read and write geometry. As shown in the previous paragraphs, magnetic field assisted deposition of magnetic nanoparticles on such a substrate would result in rod-like particle arrangements decorating with high preference the lithographically defined magnetic tracks of the master substrate. Diameter of rods, and shape anisotropy – which may become much larger than the intrinsic anisotropies particularly in nanostrucutres -, as well as material selection would allow to tailor the key parameter of magnetic recording media [5, 32, 33]. Figure 5 illustrates the two-step process suggested to prepare nanoscale perpendicular magnetic storage media.



Fig. 5. Manufacturing process of a perpendicular magnetic storage medium by magnetic field directed self-assembly. (a) Schematic topview of a perpendicular magnetic storage medium master substrate which is a prerequisite for high throughput mass production. A cross-sectional view of the marked rectangular frame in (a) is shown in (b). (b) Lithographically generated high permeability (high μ_r) tracks. The buffer layer enables to lift off the deposit from the master substrate. In what follows, we describe the steps necessary to build-up the magnetic storage medium: Step 1 (c), magnetic field assisted deposition of magnetic aerosol particles forming nanorods by sintering. Step 2 (d), mechanical stabilisation and chemical passivation by a filler material. Step 3 (e), attachment of a carrier substrate on the magnetic storage layer. Step 4 (f), perpendicular magnetic storage medium lifted off from the master substrate.

4. Ferrofluids (FF)

Interestingly, the impact of tailor-made magnetic nanoparticles has not only influenced the development of novel solid state nanostructures and devices but also the realm of complex fluids has benefitted from the availability of an ever growing variety of magnetic nanoparticles. Ferrofluids (FF) [34] manifest a scientifically and commercially relevant example of a smart complex fluid, consisting of magnetic nanoparticles, typically spherically-shaped, with diameters on the order of 10 nm and with adsorbed dispersant layers of approximately 1-2 nm thickness, enabling to stably immerse such particles in nonmagnetic carrier fluids. They decorate magnetic field gradients, which gave raise to a number of commercially viable applications of FF such as rotary seals, stepper motor dampers or heat transfer fluids in audio speakers. Owing to the possibilities for designing and modifying the physical and chemical properties of both the suspending fluid and the particles as well as the adsorbed dispersant layer, FF are gaining popularity in several novel applications, functioning as magneto-responsive colloidal extractants, targeted magnetic carriers, in vivo imaging agents and in magnetic cell-sorting schemes [35]. Those nanoparticles represent either permanent magnets, or behave as superparamagnetic particles. Suspended in carrier fluids, they undergo rotational and translational Brownian motion. The free rotation of magnetically hard particles in a carrier liquid exhibits a magnetization versus field behavior resembling that of superparamagnetic particles, yet is of different origin. It is the fascinating interplay between magnetic and rheological properties that has generated much cross-disciplinary interest in the nature and behavior of FF [36].

A central issue of fundamental research on FF is magnetoviscosity, discovered by McTague and Rosensweig et al. [37, 38], delineating that in the presence of a homogeneous magnetic field the magnetic torque on magnetically hard particles hampers or even prevents them from free rotation in a shear flow as dictated by the fluid dynamics of the carrier liquid. By taking into account the magnetic and mechanical torques as well as the thermally induced Brownian motion, Shliomis [39] delivered the first theoretical description of the magnetoviscous effect for a FF in the dilute regime of magnetically non-interacting, spherical particles. As a result, the viscosity rises with increasing magnetic field H and the relative viscosity $\Delta n/n_0$ reaches a plateau-value of 1.5 ϕ , where $\eta_0 = \eta(H = 0)$, and ϕ is the nanoparticle volume fraction. Recently, Odenbach and coworkers [40] investigated the magnetoviscous behavior of highly concentrated ($\phi \gtrsim 0.1$), commercially available FF and found changes of viscosity more than a hundred times larger than the values expected from theory [41]. It has been verified that this dramatic increase of viscosity is due to dipolar-interaction-driven formation of chain-like aggregates of individual particles. A second observation manifests that with increasing shear rates, $\dot{\gamma} \gtrsim 10 \, \text{s}^{-1}$, the giant viscosity enhancement disappears, which has been attributed to the fragile nature of the dipolar coupled chain-like aggregates; in fact, it has been suggested that they become disintegrated by shear forces supplied by the carrier fluid [42].

Irrespective of fundamental research issues, the envisioned novel applications or the diversity of commercially viable applications of FF, the currently used FF manifest a common characteristic: namely, the spherical/equiaxed shape of the constituent magnetic particles. Regarding their magnetic properties, the effect of strength of the magnetocrystalline anisotropy energy on the magnetoviscosity has been theoretically investigated quite recently [43]. We propose to explore a plausible, yet heretofore scarcely noticed degree of freedom: the *shape-anisotropy* of the constituent particles, which can be tailored to enhance various FF-properties. In particular, we will prepare and characterize rod-like magnetic nanoparticles, which behave as Brownian particles when immersed in a carrier fluid, therefore, named: nanorod-FF. The rod-like instead of sphere-like geometry of the magnetic phase, first, suppresses superparamagnetism as well as typically overcomes the crystalline anisotropy of the particles due to the large shape anisotropy energy and, secondly, anisometric permanent magnets with solid-like rigidity are expected to resist shear flow and hence contribute to magnetoviscosity far more effectively than equiaxed particles.

4.1 Nanorod ferrofluids: basic ideas

Based on a Fokker–Planck equation, Martsenyuk, Raikher and Shliomis [44] derived an expression for the magnetic-field-dependent change of viscosity, $\Delta \eta$, of a dispersion of non-interacting nanoparticles exposed to homogeneous shear flow, given as:

$$\Delta \eta = \frac{1}{4} \phi \, \tau_{\perp} M(B) \, B \,. \tag{15}$$

The applied magnetic field is labeled by *B*, the transversal relaxation time τ_{\perp} translates into the Brownian relaxation time $\tau_{\rm B}$ via $\tau_{\perp} = 2\tau_{\rm B}/(2 + \xi L(\xi))$ where *L* denotes the Langevin function $L(\xi) = \operatorname{coth}(\xi) - 1/\xi$ with its argument $\xi = mB/k_{\rm B}T$, and m stands for the magnetic moment of an individual particle. M(B) indicates the field-dependent magnetization of the FF which for small shear flow according to [44] may be approximated by $M(B) = M_s L(\xi)$ and $M_s = m^{\text{tot}}/V_{\text{mag}}$ is the saturation magnetization of the sample. The overall number of particles making up the magnetic volume V_{mag} and occupying the volume fraction ϕ of the FF have the overall magnetic moment m^{tot} . It seems instructive to consider the limiting case of saturation, where a sufficiently large applied field, B_{sat} , assures that the Langevin function approaches a quasi-plateau-value characterized by the saturation magnetization M_s . It is straightforward to derive that by approaching saturation at fixed temperature *T*, say room temperature, Eq. (15) simplifies to

$$\Delta \eta(B_{\rm sat}) \propto \phi \,\tau_{\rm B} \,. \tag{16}$$

The particle geometry is hidden in $\tau_{\rm B} = (2D_n)^{-1}$, with D_n being the coefficient of rotational diffusion. As shown by Brenner [45, 46], D_n of solids of revolution – here we consider long slender axisymmetric bodies, *e.g.* cylinders – can be written as:

$$\frac{1}{D_n} = \frac{K(n)}{D_s},\tag{17}$$

where K(n) is a shape function, *n* specifies the aspect ratio of bodies and $D_s = k_B T/6 \eta V_{hyd}^s$ is the Stokes rotational diffusion coefficient of a sphere with equal hydrodynamic volume, $V_{hyd}^s \equiv V_{hyd}^{cyl}$. Mathematical expressions for shape functions are given in references [45–49]. For the sake of argument, it seems sufficient to display the functional form of K(n) as shown in Fig. (6) for prolate ellipsoids and circular cylinders [45, 46], where

$$K(n) = \frac{2}{9} \left[\frac{n^2}{\ln n} + \frac{n^2}{(\ln n)^2} (\ln 2 - 1) + \frac{3L}{8\pi} \right]$$
(18)

denotes the shape function of a blunt-ended cylinder with aspect ratio n. The numerical constant L depends critically on the precise shape of the blunt ends



Fig. 6. Shape function K(n). Functional behavior of K(n) versus aspect ratio n for cylinders (dashed line) and prolate ellipsoids (full line).

of the body; $L \approx 5.45$ has been determined for a circular cylinder. Requiring $V_{hyd}^s \equiv V_{hyd}^{cyl}(n)$ and substituting Eq. (18) into Eq. (17) yields an expression for the rotational diffusion coefficient and, hence, also for τ_B which depends apart from temperature on the material parameters η , M_s , ϕ and n. Let us consider spheres (n = 1) as reference system, and further assume that all material parameters except n are fixed at constant temperature. Then, increasing n at conserved V_{hyd}^s consequently contributes with a nonlinear enhancement of τ_B and thus $\Delta \eta$ due to the effect of shape anisotropy on D_n imparted by K(n). We note that $\tau_B = (1/2\pi) f_B^{-1}$ is inversely proportional to the Brownian relaxation frequency f_B , which is quantitatively accessible by means of ac-susceptibility measurements. This allows one to deduce an overall aspect-ratio of anisometric objects, probed in the state of being immersed in a carrier fluid, based on the relation

$$\frac{1}{f_{\rm B}(n)} = \frac{\pi K(n)}{D_{\rm s}},\tag{19}$$

provided that all other material parameters are prescribed. Finally, since $f_{\rm B}(n)$ renders τ_{\perp} becoming *n*-dependent, the magnetic-field-dependent viscosity of nanorod FF [Eq. (15)] is suggested to crucially rely upon *n*, which, when exceeding 10, may give rise to a *giant magnetoviscous effect*. We will scrutinize this expectation by performing field and frequency dependent viscosity measurements on a nanorod FF in a squeeze flow rheometer.

4.2 Synthesis and characterization

Iron nanorods were generated in a modified aerosol flow condenser [50] as shown in Fig. 7. Before evaporation, the reactor was evacuated to 10^{-6} mbar. Then the high vacuum pump was disconnected and replaced by a rotary vane



Fig. 7. Magnetic-field-assisted aerosol synthesis of Fe-nanorods. Iron particles are grown in an Ar gas flux and become linearly aligned in the presence of a homogeneous magnetic field. Sintering promotes rigid nanorod formation. Oleic acid is evaporated as a surfactant to avoid agglomeration between as-grown nanorods. Further downstream the oleic-acid-coated nanorods are collected on a cold finger held at 77 K.

pump in order to establish a continuous Argon gas flow of 40 sccm reading a pressure of 20 mbar. Elemental iron was heated and evaporated from a tungsten crucible into the Argon gas flux using an induction coil operated at a frequency of 700 kHz and a maximum power output of 20 kW. Supersaturation of Fe in the Ar gas leads to nucleation of Fe clusters. Subsequent growth by condensation and coagulation results in Fe-nanoparticles which further downstream tend to form, depending on their local density in the gas phase, particle aggregates - dimers, trimers, etc. Since the evaporator was located in the homogeneous field regime at the entrance of a Halbach-type permanent magnet, linear aggregation of individual nanoparticles becomes strongly favored. First, due to the magnetic torque experienced by all nanoparticles, which make their magnetic moments rotate parallel to the field direction. Whenever the magnetic torque couples sufficiently strong to an easy axis and/or the shape of the particles, it impels a rotation of these particles themselves. Secondly, owing to the dipolar interaction which favors a head-to-tail arrangement of particulate dipoles among all other possible configurations, the emergence of linear particle aggregates seems highly reasonable. The enhanced temperature extending along the Halbach magnet enables sintering [18] of these anisometric particle aggregates along their way downstream. It is the reduction of the particles free surface energy that yields the driving force for sintering, which causes neck formation between neighboring particles resulting in rod-like magnetic objects with solid-like rigidity, concisely called nanorods.

In order to prevent agglomeration of already grown nanorods in the Ar gas, we coated individual nanorods by evaporation of oleic acid using a thermally heated quartz glass crucible placed at the exit of the Halbach magnet. Variation of the distance between the rf coil and the surfactant source allowed us to roughly control the rod length: a shorter rod length appeared when decreasing this distance. The aerosol jet exiting the Halbach magnet is directed toward a LN₂ cooled cold finger where the oleic acid coated nanorods become deposited due to thermophoresis. After turning off the evaporation sources, the Ar gas flux was still maintained until the cold finger temperature approached room temperature. Then the Ar gas pressure was increased to ambient pressure and via a leak valve Ar gas was slowly exchanged by air in order to passivate the surface of the oleic acid coated nanorods by a thin oxide layer thus avoiding full oxidation of available iron and rendering the samples appropriate for handling under atmospheric conditions. The soot-like material collected on the cold finger was rinsed off using heptane and accumulated in a container. Adding a polar solvent (acetone) makes the oleic-acid-coated particles to agglomerate, which allows then to separate them from the solvent by using a permanent magnet. Repeated redispersing of the coated particles in heptane and separation eventually leads to a stable FF. The volume concentration of the magnetic phase immersed in the carrier fluid was determined by magnetometry yielding the magnetic moment which is directly proportional to the volume of magnetic objects whenever they become saturated through an applied field. We preferred to prepare FF with a volume concentration of magnetic phase of 1-2 vol.-% to assure that such FF agree with the limiting case of a dilute, non-interacting system. The structure and morphology of nanorods has been investigated by means of TEM (Jeol JEM 2010).

As discussed in the theory section, the Brownian relaxation frequency $f_{\rm B}$, which enables access to the aspect ratio, is related to the complex acsusceptibility $\chi(f)$. In fact, $f_{\rm B}$ coincides with the frequency f correlated to the maximum value of the imaginary part $\chi''(f)$ of $\chi(f) = \chi'(f) + i\chi''(f)$. Using a Quantum Design PPMS (Model 6000), we measured $\chi(f, T)$ and also obtained $\chi''(f, T)$ by means of sinusoidally varying the applied magnetic field between ± 10 Oe at frequencies covering the range between $10-10^4$ Hz.

The magnetoviscous behavior of nanorod FF has been investigated by utilizing a PAV (piezo-axial-vibrator) rheometer [51]. The specimen chamber has a disc-shaped geometry of 20 mm diameter, a height of 5 μ m and can be operated under closed-system conditions. The bottom part of the chamber is designed to act as a piezo-driven membrane vibrating at frequency f and an amplitude of 5 nm in this way forcing the nanorod FF to sustain dynamical squeeze-flow. The frequency-dependent viscosity is deduced from the complex spring constant of the vibrating system [52]. Using a solenoid oriented with its axis perpendicular to the driving membrane, a magnetic dc-field of variable strength can be applied to the specimen chamber.

4.3 Results and discussion

In Fig. 8 we show a representative bright field micrograph of an assemblage of nanorods prepared by the magnetic-field-assisted aerosol process discussed in the previous paragraph. A statistical evaluation of the geometry of objects was, in general, hampered by the circumstance that they exhibited a strong tendency



Fig. 8. Morphology of nanorods. Representative TEM bright field micrographs of aerosolgrown nanorods at low (a) and high (b) magnifications.



Fig. 9. Neck formation and iron-oxide core shell structure. (a) TEM dark field image displaying intergrain neck formation. (b) TEM dark field micrograph revealing the existence of a thin oxide layer, marked by arrows, surrounding the Fe-core of grain 2.

to agglomerate during preparation of the TEM specimen, so causing projection artefacts which in turn gave rise to high uncertainty of the values determined for their individual length. This problem is due to attractive magnetic dipolar forces between individual rods which tend to impel agglomeration as the solvent evaporates. As a consequence, we restrict our analysis to estimating the overall diameter of nanorods; an effective aspect ratio of nanorods will be obtained from the ac-susceptibility as shown in the next paragraph. TEM micrographs displayed in Fig. 9 reveal clear evidence for neck formation between individual particles – so providing the nanorods with rigidity – and the formation of a thin oxide layer protecting the core volume of particles/nanorods from further oxidation. The ac-susceptibility measurements allowed to deduce the imaginary part $\chi''(f)$ of the complex susceptibility of a nanorod FF. The



Fig. 10. Ac-susceptibility of a nanorod FF. Imaginary part of the susceptibility of a nanorod FF at 4 different temperatures and $H_{dc} = 0$. The different lines represent fits to the data points using Eq. (20). The data set taken at T = 150 K displays the signal of a frozen fluid, indicating that Brownian relaxation is missing. Brownian relaxation frequencies can be deduced from the maxima of the upper three curves.

experimental data shown in Fig. 10 were analyzed in terms of the Cole–Cole model [53]

$$\chi''(2\pi f) = \frac{\chi_0 - \chi_\infty}{2} \left(\frac{\sin\left(\frac{\pi\beta}{2}\right)}{\cosh\left(\beta \ln\left(2\pi f\tau_{\rm CC}\right)\right) + \cos\left(\frac{\pi\beta}{2}\right)} \right),\tag{20}$$

which could fit all data points and yielded the frequencies $f_{\rm B}$ associated with the maximum values of $\chi''(f)$. The Cole–Cole model represents an empirical modification of the Debye-relaxation. The parameter β has been introduced as a measure of the width of a size distribution of individual objects exposed to the ac-field and $\tau_{\rm CC}$ denotes the average relaxation time. According to Eq. (19), determination of the effective aspect ratio, $n_{\rm eff}$, based on experimental data for $f_{\rm B}(n)$ relies upon a reasonable approximation to the geometry of nanorods. For the sake of simplicity, we assume a cylinder geometry so implying $V_{\rm hyd}^{\rm nrod}(n) \approx$ $V_{\rm hyd}^{\rm cyl}(n)$. The hydrodynamic nanorod volume is modeled by

$$V_{\rm hvd}^{\rm nrod} \approx (\pi (r+t)^2)(n2r+2t), \qquad (21)$$

where *t* is a measure of the thickness of the surfactant layer (oleic acid) bonded to the solid core-structure of the nanorods, *r* is the rod diameter and *n* is the aspect ratio representing the number of spheres of diameter 2r that would fit into the hollow cylinder with an inner radius of *r* and an outer radius of (r + t). Concerning further data analysis, we fixed $r \simeq 5$ nm based on TEM results, and supposed *t* is reasonably approximated by a monolayer of oleic acid having a thickness of 1–1.5 nm. We note that the data shown in Fig. 10 suggest that the onset of Brownian relaxation should correlate with the melting transition of the carrier fluid; below the melting point, Brownian relaxation



Fig. 11. Aspect ratio deduced from the temperature-dependent ac-susceptibility. Pseudo-3d chart of the imaginary susceptibility $\chi''(f, T)$ of a nanorod-FF at $H_{dc} = 0$ [see Fig. 10]. Black dots (•) indicate maximum values of χ'' characteristic of Brownian relaxation frequencies. Full lines show computed relaxation frequencies for different aspect ratios *n* and a nanorod diameter d = 11 nm, representing an average diameter obtained from TEM for the investigated nanorod-FF. The vertical line at T = 183 K indicates the melting point of the carrier fluid heptane.

should cease. Any signal in this regime would originate from superparamagnetic (Neelian) relaxation [54]. In order to verify this conjecture, we measured frequency- and temperature-dependent ac-susceptibilities to obtain $\chi''(f, T)$ as shown in Fig. 11. It is straightforward now to analyze the maximum of $\chi''(f, T)$ in terms of $f_{\rm B}(n, T)$ where n is treated as a parameter, implying that $V_{\rm hvd}^{\rm s}$ in $D_{\rm s}$ is substituted by $V_{\rm hvd}^{\rm nrod}(n)$. The temperature dependence of $f_{\rm B}$ reveals the temperature dependence of the rotational diffusion coefficient. The Brownian relaxation frequencies derived from the Cole-Cole analysis are depicted as black dots. The full lines are fits to the data points using Eq. (19). Superparamagnetic relaxation below $T_{\rm M}$ seems absent. For integer values of n, it is shown that n = 24 is a fairly good approximation to the data points. In this context n is characteristic of an effective aspect ratio, $n_{\rm eff}$, ensemble-averaged over an *a pri*ori unknown distribution of geometrical/morphological degrees of freedom of nanorods probed by $\chi''(f, T)$. We found that *n* does not depend on temperature and frequency. What is more, we also verified that *n* is independent of the magnitude of a superimposed magnetic dc-field. Dc-bias-fields were successively applied up to a magnitude of 20 mT and, as suggested by Waldron et al. [55], we observed for all fields applied only a shift of the relaxation frequency, however, no concomitant change of n. The fairly large value of n seems to indicate that among all others the largest nanorods may control the overall behavior of the complex fluid. We conclude by pointing out that all observations made so far imply that nanorods manifest a pronounced aspect ratio in conjunction with solid-like rigidity.

The effect of shape anisotropy on the magnetoviscous behavior of nanorod-FF has been investigated by utilizing a PAV (piezo-axial-vibrator) rheome-



Fig. 12. Magnetoviscous effect of a nanorod FF. (a) Magnetic field dependent viscosity change as obtained from a PAV viscosimeter at different frequencies. Lines represent least squares fits to the experimental data based on Eq. (15). The volume concentration of the magnetic phase corresponds to $\phi = 0.9$ vol.- ∞ . (b) Frequency-dependent viscosity change for different magnetic fields. Full lines reflect least squares fits based on Eq. (20). The shift of maxima to higher frequencies with increasing field strength indicates a deviation from pure orientational relaxation behavior.

ter [51]. In Fig. 12 we display the relative change of viscosity of a nanorod-FF as a function of applied field and frequency, respectively. With the volume fraction ϕ of the magnetic phase determined by magnetometry to be 0.9 vol.-‰ – assuming that all magnetic material is made up of Fe – we analyzed the data points shown in Fig. 12a in terms of Eq. (15). The full lines depict a least squares fit with τ_{\perp} being the central fit parameter. Fig. 12b reveals a magnetic field-dependent shift of maxima of $\Delta \eta/\eta_0$ to higher frequencies with increasing field strength; the fit to the data points is based on the Cole–Cole formula, Eq. (20). This shift supports the idea that, apart from mere orientational relaxation behavior of the nanorods, resonance behavior becomes superimposed with the applied homogeneous magnetic field acting as the restoring torque.

Finally, we compare the magnetoviscous effect of nanorod FF with conventional commercially available FF. In order to make this comparison convincing, we normalize the relative change of viscosity to the volume fraction ϕ of the magnetic phase immersed in the carrier fluid. In Fig. 13 the quantity $\Delta \eta/\phi\eta_0$ for a conventional FF, investigated by Odenbach and coworkers, is contrasted with the nanorod FF. A direct comparison of the two sets of data would require a relation between the shear-rate- and frequency-dependent viscosity. Although there is no general theory describing the relation between $\eta(\dot{\gamma})$ and $\eta(f)$, for simple liquids the Cox–Merz theorem postulates in its rigorous version $\eta(\dot{\gamma}) = |\eta^*(f)|$, where $\eta^*(f)$ is the complex viscosity; for complex fluids this identity brakes down. Recently, Chae *et al.* [56] investigated the validity of the Cox–Merz rule for magnetic dispersions. They could demonstrate



Fig. 13. Shear-rate- and frequency-dependent magnetoviscous effect of a conventional and a nanorod-FF. Full black symbols denote the conventional, highly concentrated FF and open symbols characterize the nanorod-FF. The relative viscosity change is normalized to the volume fraction ϕ of magnetic phase. Frequency values can be translated into shear rates through division by 10 for direct comparison.

that the slopes of the viscosity and the complex viscosity as a function of $\dot{\gamma}$ or f, respectively, are nearly identical. When they shifted the frequency by a slightly concentration dependent but otherwise constant factor $a \approx 0.1$, they found the relation $\eta(\dot{\gamma}) \approx |\eta^*(a f)|$ reasonably good obeyed. Therefore, by dividing the frequencies given in Fig. 13 by a factor of 10, the viscosity data of the nanorod FF and the conventional FF are expected to be comparable on a one to one basis. A certainly striking feature is that $\Delta \eta / \phi \eta_0$ of conventional FF exhibits a decrease over two orders of magnitude with increasing shear rate, whereas, only little change was detected for nanorod FF. In detail, at a shear rate of 10^{-1} s⁻¹ and raising field strength, $\Delta \eta / \phi \eta_0$ of conventional FF reveals a restrained increase (concave-up), in contrary, the nanorod FF is characterized by a pronounced enhancement up to virtually saturation behavior within less than 10 mT of applied field. Such a behavior is in agreement with the idea that in conventional FF, with the given high volume fraction $\phi \gtrsim 0.1$ of magnetic phase, raising field strength triggers chain formation of dipolar interacting nanoparticles, and growing chain length goes along with an increase in $\Delta \eta / \phi \eta_0$ [40]. On the other hand, the solid-like rigidity of nanorods, which are present in the carrier fluid also at zero field, makes this complex fluid susceptible to small applied fields ($B \lesssim 10 \,\mathrm{mT}$) and as a consequence results in a concomitant severe change of $\Delta \eta / \phi \eta_0$. In the shear rate or frequency regime which is of technical relevance $(\dot{\gamma}, f \gtrsim 10 \,\text{s}^{-1}), \Delta \eta / \phi \eta_0$ of the conventional FF drops by two orders of magnitude, in contrast to the nanorod-FF which yields evidence for, on that scale, a nearly frequency-independent behavior. As conjectured, the solid-like rigidity of nanorods renders them resistant against mechanical forces/torque mediated by the fluid phase. By contrast, the applied-field-enhanced build-up of dipolar coupled chain-like aggregates in

conventional FF results in shear unstable objects, which become basically disintegrated into their individual building blocks whenever the shear rate exceeds 10 s^{-1} .

In summary, we succeeded in preparing a nanorod-FF, a complex fluid made up of shape-anisotropic magnetic particles – called nanorods – immersed in a nonmagnetic carrier fluid. These anisometric permanent dipoles have solid-like rigidity and behave as Brownian particles. Nanorod-FF manifest a giant magnetoviscous effect, particularly, in the low field regime (≤ 10 mT) and at measured frequencies/shear rates up to $10^3/10^2$ s⁻¹. Therefore, nanorod-FF recommend themselves as a novel class of complex fluids with a major potential for technical applications. Since the magnetoviscous effect can be "switched on" at low magnetic fields as well as in the regime of technical relevant shear rates, applications in the areas of microfluidics and MEMS and/or NEMS appear plausible.

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