Sharpening the surface of magnetic paranematic droplets†

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In a non-uniform magnetic field, the droplets of colloids of nickel nanorods and nanobeads aggregate to form a cusp at the droplet surface not deforming the entire droplet shape. When the field is removed, nanorods diffuse away and the cusp disappears. Spherical particles can form cusps in a similar way, but they stay aggregated after the release of the field; finally, the aggregates settle down to the bottom of the drop. The X-ray phase contrast imaging reveals that nanorods in the cusps stay parallel to each other without visible spatial order of their centers of mass. The formation of cusps can be explained with a model that includes magnetostatic and surface tension forces. The discovered possibility of controlled assembly and quenching of nanorod orientation under the cusped liquid surface offers vast opportunities for alignment of carbon nanotubes, nanowires and nanoscrolls, prior to spinning them into superstrong and multifunctional fibers. Magnetostatic and electrostatic analogies suggest that a similar ideal alignment can be achieved with the rod-like dipoles subject to a strong electric field.

Introduction

With progress in nanotechnology, nanoparticles are finding new applications beyond their traditional use in paints, coatings, foods, drugs, and cosmetic products. Rod-like nanoparticles dispersed in a host fluid deserve special attention because of their specific anisotropic interactions leading to transformation of these colloidal suspensions into colloidal liquid crystals with unique properties.1–4 Traditional applications of colloidal liquid crystals are currently significantly extended to include precursors for multifunctional composites and fibers.5–14 Ordering of rod-like nanoparticles inside the fiber precursor jet is a challenge: attractive van der Waals interactions among the particles lead to the particle clustering followed by separation from the host fluid. Stabilization of dispersions is achieved through physico-chemical functionalization of nanoparticles to counterbalance attractive forces by coulombic, steric, or other repulsive interactions. The delicate balance between attractive and repulsive colloidal interactions can fail when the jet comes out from the meniscus and other forces enter the game.7–9

Here we report on the development of a physical principle of an almost ideal alignment of magnetic nanorods under the free liquid surface. Due to magneto-static interactions between magnetic nanorods, they can be gathered on demand within a

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3sm52655k

Received 15th October 2013
Accepted 27th November 2013
DOI: 10.1039/c3sm52655k
www.rsc.org/softmatter

Fig. 1 (a) A schematic of the experimental setup used in the X-ray phase contrast imaging experiment; the field distribution is specified by the magnetic flux lines calculated numerically with FEMM (http://www.femm.info). (b–e): X-ray phase-contrast images of the droplet at various distances l from the magnet to the droplet. (f) Axial magnetic field $B_z$ measured experimentally and calculated numerically with FEMM vs. distance l from the magnet, point l = 0 corresponds to a central point at the magnet surface. (g) Radial component of the magnetic field $B_r$ calculated along the vertical dashed lines shown in (a).
fraction of a second by applying a magnetic field gradient. Since
the nanorod length is measured in tens of microns, only
hundreds of nanorods are needed to form a millimeter long
chain. Such long chains can be formed with milliTesla magnetic
fields (<0.035 T) (Fig. 1b).\textsuperscript{15–18} The formation time of a micron
size magnetic cluster can be made comparable or even shorter
than that of a commercial printing device. Therefore, the sug-
gested physical principle is of industrial importance and can be
used for formation of magnetic fibers\textsuperscript{12–14} and for printing
magnetic droplets.\textsuperscript{15–18}

Results and discussion

Behavior of nanorods in the droplet

A colloidal suspension of nickel nanorods of 200 nm in diam-
eter and 20 μm in length was prepared in ethylene glycol as
described in ref. 19 and 20 and in the Materials and methods
section. A study of the nanorod clustering was performed using
the X-ray phase contrast imaging at the Advanced Photon
Source at Argonne National Laboratory, IL, with a beam energy
of 33.2 keV. A schematic of the experimental setup is shown in
Fig. 1a and a sequence of pictures illustrating the behavior of
nanorods in a magnetic field is presented in Fig. 1b–e. We
moved the magnet toward the droplet with a constant speed
$(V = 0.2 \text{ mm s}^{-1})$. Fig. 1b–e show the droplet configuration
and the structure of visible nanorod chains and clusters at different
distances $l$ from the magnet (see Video S1†). These visible
chains and bundles ($\sim300 \mu \text{m long}$) are formed at a very weak
milliTesla range field. When the magnet is far away from the
drop, the field is almost uniform and all nanorod bundles are
distributed evenly over the droplet volume (Fig. 1b). The mag-
netic field orients the nanorods in the vertical direction, but
the nanorods are free to move presumably forming a para-
nematic-type liquid crystal\textsuperscript{9} where the crystal elasticity is mostly
caused by the long range dipole–dipole interactions between
nanorods.\textsuperscript{21–26} As the magnet moves closer to the droplet,
the nanorods form long chains from the droplet bottom to the top
free surface. When the magnet is in close proximity to the drop,
producing a strong field gradient, these chains and strands
come together to form a cluster concentrated at the droplet axis
of symmetry near the droplet surface. The explanation of the
assembly of magnetic nanorods and chains is as follows.

Nickel nanorods show an almost zero magnetic moment in
the absence of a magnetic field and acquire a magnetic moment
linearly dependent on the field when the field is less than 0.1 T
(Fig. 2). The magnetostatic energy of two magnetic dipoles
oriented in the head-to-tail configuration is half of that
observed in the configuration when the dipoles are placed side
by side.\textsuperscript{22,27} Therefore, the distant nanorods have a tendency
to form chains. Two parallel nanorods are prone not only to the
head-to-tail ordering, but they have a tendency of sidewise
attraction as well.\textsuperscript{28} Therefore, the nanorods have a tendency
to cluster in strands or bundles right after the application of a
magnetic field. When the nanorods are subject to a gradient
field, one more mechanism of their clustering has to be
considered. In a gradient field, the magnetic force acting on a
nanorod is written as $F_m = (\mathbf{m} \cdot \nabla) \mathbf{B} = -(m_z \partial / \partial z) \mathbf{B}$ where $m_z$ is a

magnetic moment of the nanorod and $\mathbf{B}$ is the magnetic field
vector. The “minus” sign takes into account the fact that the
magnetic moment is pointed in the negative direction of the
$z$-axis. Therefore, the direction of the radial component of the
magnetic force causing the nanorods to cluster at the central
axis or spread away from it depends on the $z$-derivatives of the $B_z$
field component. This radial field component is directed toward
the central axis, \textit{i.e.} it is negative, and it fades away as the
$z$-coordinate increases (Fig. 1g). Accordingly, the radial
component of the magnetic force is negative pushing the
nanorods to cluster at the central axis. As follows from Fig. 1f,
the $z$-derivative of the vertical component of the magnetic field
is positive. Therefore, the $z$-component of the magnetic force
is negative: it tends to bring all nanorods to the top. These argu-
ments explain the phenomenon of nanorod clustering at the top
of the droplet closer to its central axis. The same arguments are
applied to explain the clustering of colloids of magnetic beads
forming chains behaving like nanorods in a magnetic field.

Deformation of the particle laden droplets in non-uniform
fields

As the cluster size increases, it deforms the droplet by creating
a sharp peak at the top (Fig. 1d and 3b). The rest of the droplet
profile remains non-perturbed. The process of nanorod
agglomeration with cusp formation in the droplets shown in
Fig. 1b–d is reversible: when the magnet is removed, the
nanorods diffuse away and the droplets take on the original
shapes. Remarkably, the entire droplet shape does not change
during the cusping of its pole; the droplet deforms like a poppy head of the Orthodox Church.

When the magnet is moved to some critical distance closer to the droplet, the cluster breaks and a daughter droplet jumps towards the magnet. The cluster breakup cannot be prevented even if the magnet is first brought to the critical distance and then is immediately moved away. The image in Fig. 1e shows the drop profile when the cluster is about to leave the drop.

This point-like local deformation of the nanorod-laden droplets is very unusual and has never been documented in the literature on colloids of magnetic nanobeads, known as ferrofluids.27,29–31 The published experimental observations on ferrofluid droplets deal with a uniform magnetic field.29–32 In this case, the entire droplet deforms as shown in Fig. 3e and f. The phenomenon of cusp formation on the surfaces of ferrofluid droplets subject to a uniform magnetic field is known as the Rosensweig instability.27 However, the localization of this cusp and isolation of a cluster of magnetic nanoparticles at the droplet apex are specific only for a non-uniform magnetic field. The Rosensweig instability has been studied in detail in the past.27,29–35 It appears that the drop behavior in a uniform magnetic field is very much similar to the behavior of dielectric droplets exposed to an electric field.33–35 Some specific features are attributed to a nonlinear relationship between droplet magnetization and the applied field.31

In order to see whether only nanorods form a localized cusp at the droplet surface, we studied the behavior of droplets from Ni nanobeads. Different diameters of nanoparticles have been used in these experiments: 30 nm, 165 nm and 605 nm (Fig. 4). The concentration of nanobeads was kept the same as that in the experiments with Ni nanorods of 200 nm diameter. Similar poppy heads were obtained even for the smallest studied concentrations of nanoparticles (Fig. 5). The main difference between nanorods and nanobeads documented experimentally is that when the magnetic field is removed, nanobeads sink down while maintaining the cluster structure whereas in the
case of nanorods, nanorods stay at the drop interface and diffuse away (Fig. S3†). All these experiments suggest that the cusp localization and isolation of a cluster of magnetic nanoparticles at the drop apex is specific only for a non-uniform magnetic field.

This difference in nanoparticle clustering is not completely understood. We suggest the following hypothesis based on a significant difference in the field distribution around uniformly magnetized nanorods and beads. Long nanorods interact through their poles, i.e. through their “magnetic charges” with the energy of two poles inversely proportional to the distance between them.26 Short nanorods interact as nanobeads, i.e. as dipoles.27 As follows from the phase diagram of two nanorods,28 the greater the nanorod length-to-diameter ratio, the greater the zone of their repulsion. Therefore the aligned nanorods at the outmost interfacial layer are held together mostly by the field gradient. When the field is released, the sidewise repulsion of the nanorods forces the cluster to break apart and the thermal excitations help nanorods to diffuse away.28 The phase diagram for two nanobeads reveals a larger area of the attraction zone: where the nanorods of finite length repel each other, the nanobeads of the same magnetization can come together.28 Therefore, in contrast to the nanorods, the self-assembly of magnetic beads in an external magnetic field often proceeds via 1D (chain), 2D (sheets) to 3D structures.37,38

Clusters of magnetic beads are very difficult to destroy,39-43 most likely, because even after removal of the external field, the dipoles self-support the structure due to their internal field. In addition to the dipole–dipole interactions, magnetic beads are faceted, as shown in Fig. 4. Therefore, these beads are expected to experience strong van der Waals interactions keeping them together.

**Forces responsible for the cluster stability**

Except for the structure of nanoparticle packing in the cluster, the behavior of poppy heads for different colloids is very much similar. Therefore, we hypothesized that only capillary, gravitational, and magnetic forces are crucial for cusping the droplets. Fig. 1e shows the first irreversible shape of the nanorod laden droplet at a critical distance $l$. At this moment, the whole cluster filled with magnetic nanorods detaches from the mother droplet and jumps toward the magnet. This is a manifestation of an interfacial instability when the surface tension is unable to support the surface deformations and any infinitesimal perturbation of the surface results in an eruption of the droplet interior.44 A similar behavior of magnetic cusps was observed with the nanobead droplets. Therefore, we assume that the structural elasticity of magnetic aggregates plays no role and the cluster acts like a solid magnetic body pulling the droplet surface toward the magnet. Estimation of the Bond number, $Bo = \frac{g\rho R^2}{\sigma}$ ($R$ is the radius of the droplet and $\sigma$ is the surface tension), revealed that it is less than 1; hence gravity is insignificant in these experiments. Thus the drop shape is controlled mostly by the capillary forces; these forces counterbalance the magnetic force pulling the droplet at the cusp. Therefore, the droplet profile excluding the cusped pole is expected to be similar to an equilibrium unduloid describing the shape of a droplet sitting on a wire, as shown in Fig. 3c and d.46 In the drop-on-a-wire model, the unduloid is pulled in the opposite direction by the interfacial tension of the wire surface acting at the contact lines.

The unduloid corresponding to the given droplet is a solution of the Laplace equation of capillarity;45 it is defined by a function $f(r, x1/L, x2/L, \beta)$ where $r$ is the wire radius, $x1$ is the droplet radius, $L$ is the droplet length, and $\beta$ is the contact angle (see the definitions in Fig. 3d and the ESI for the analysis†). By adjusting the contact angle $\beta$ and the droplet height $L$, one can fit the droplet shape.

In order to confirm this analogy, the magnet was removed and different wires with diameters in the range between 0.07 mm < $d$ < 1.5 mm were brought into contact with the droplet. We examined copper wires with diameters $d = 0.4$, 0.8, 0.85, 1 and 1.5 mm, tungsten wires with $d = 0.127$ and 0.07 mm, and stainless steel wires with $d = 1$, 0.8 and 0.46 mm. Only upon immersion of a stainless steel wire with $d = 0.46$ mm, we observed an unduloid, the solid line in Fig. 3c, which was identical to that shown in Fig. 3b corresponding to the droplet shape at the onset of instability. Seven droplets with different nanorod concentrations were analyzed to obtain an apparent contact angle using Carroll’s solution. In all cases we found that the angle was constant $\beta = 49° \pm 0.7°$ ($n = 7$ droplets).

**Critical conditions for detachment of magnetic clusters**

This independency of the apparent contact angle on nanorod concentration and hence on cusp magnetization is surprising and it deserves special attention. As shown in the ESI,† inside
the cusps with high magnetic permeability, the magnetostatic potential is almost constant. Therefore the description of the distribution of the magnetic field outside the cusp follows an analogous description of the distribution of the electric field outside conical conductors.66-68 The external magnetic field generates a specific distribution of magnetic poles of the same polarity at the cone-like liquid cusp. These poles repel each other and want to destroy the cone, but the capillary forces push the free surface back. This subtle competition results in a unique conical cusp with the angle $\beta = 49.3^\circ$. These liquid cones are identical to the famous Taylor cones observed on water drops and soap films, i.e. conductors.35,46 In this model, the specificity of the nanorods is not important; the same cone-like cusp was observed on the nanobead droplets; hence the model is applicable to that case as well. We discuss this electrostatic analogy in the ESI.†

Using the droplet-on-a-wire idea, one can say that the conical cusp acts as a wire pulling the droplet towards the magnet. We further confirm this hypothesis by analyzing the forces acting on the magnetic cusp. The free body diagram shown in Fig. 6a specifies these forces: magnetic forces pulling the cone toward the magnet, capillary pressure acting at the base of the magnetic cone, and surface tension forces acting at the edge of the magnetic cone.

The magnetic force exerted by the magnet is written as $F_m = (\mathbf{m} \cdot \nabla)\mathbf{B}$, where $\mathbf{m}$ is the magnetic moment of the cone. As shown in the ESI,† the nanorod magnetization in an applied magnetic field follows the linear constitutive equation, $\mathbf{m} \propto \mathbf{B}$. The measured and FEMM-calculated magnetic field can be approximated as $B_z = b/l$, $b = -0.735 \text{ mT} \cdot \text{m}$ (the dashed line in Fig. 1f). With this approximation, the magnetic force acting on the magnetic cone can be written as $F_m = abVl^2\mu_0$ where $\mu_0$ is the magnetic permeability of vacuum, $V$ is the volume of the magnetic cone, and $\alpha$ is a constant to be determined.

The surface tension $\sigma$ acting at the edge of the magnetic cone of radius $r$ results in the tensile force with the $z$-component $F_w = -2\pi r\sigma \cos(\beta)$. The rest of the droplet contributes to the free body diagram through the capillary pressure distributed over the bottom of the magnetic cone. This pressure results in the capillary force $F_c = 2\pi r^2/R$ where $R$ is the radius of the mother droplet. Collecting all forces, the force balance is represented as:

$$\frac{b^2}{l^2\mu_0} = \frac{6\sigma}{\alpha \tan \beta} \left( \frac{\cos \beta}{r^2} - \frac{1}{rR} \right)$$

(1)

In order to find the constant $\alpha$, we conducted experiments with 7 droplets of the same size ($R = 2.23 \pm 0.2$ mm) and with different initial concentrations of nanorods in the droplet (in the range from 0.043 wt% to 0.4 wt%). The cone radius $r$ shrunk as the concentration of nanorods in the initial droplets decreased (Fig. 6b and c). This decrease of the cusps size required bringing the magnet closer to it to detach the cusp. During these experiments, we measured the cone radius $r$, the distance from the peak of the droplet to the magnet, $l_{\text{cr.min}}$, and the distance from the base of the cone to the magnet, $l_{\text{cr.max}}$. The results of these experiments are shown in Fig. 6d. For each given cluster radius $r$, the circles correspond to the left hand side of eqn (1) taken at $l_{\text{cr.min}}$. The stars correspond to the left hand side of eqn (1) taken at $l_{\text{cr.max}}$. The solid line is the theoretical fit with the function $g(r) = \frac{6\sigma}{\alpha \tan \beta} \left( \frac{\cos \beta}{r^2} - \frac{1}{rR} \right)$, where $\alpha$ is an adjustable parameter. The best fit was reached for $\alpha = 0.018$.

**Materials and methods**

Nickel nanorods (200 nm × 20 μm) were produced by electrodeposition of Ni inside the pores of alumina membranes.47 Ethylene glycol was added to the beaker with nickel nanorods and after sonication for 30 seconds (Branson Sonifier 450), a uniform suspension of Ni nanorods was produced. Spherical single crystals and highly crystalline uniform Ni nanoparticles of different sizes were obtained via reduction of the nickel carbonate basic salt (The Shepherd Chemical Company) in high quality grade di-ethylene glycol (99.99% DEG). Polyol served as a reducing and dispersing agent, and as a medium. The final size of nickel particles was controlled by the limited seeding mechanism. Based on that method, dispersions with the particles of diameter $d = 30 \pm 6.1, 165 \pm 27.2,$ and $605 \pm 69.5$ nm were produced (see Fig. 4 and S1† for details on synthesis). A double sided tape (MMM237, 3M) was attached to a glass slide.

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Fig. 6 (a) Forces acting on the cluster of magnetic nanorods at a critical distance. (b and c) Cluster formed by magnetic nanorods at the top of the droplet for 2 different concentrations $c$ of nanorods in the initial droplet (b) > (c), resulting in different cluster radii $r$. (d) The solid line shows the theoretical prediction and the circles represent the calculated values of the left side in eqn (1) at $l_{\text{cr.min}}$, the stars represent the calculated values of the left side in eqn (1) at $l_{\text{cr.max}}$. Concentrations of nanorods in the droplets corresponding to the open circles are: from right to the left, wt% = 0.29, 0.24, 0.20, 0.18, 0.13, 0.10, and 0.07.
to prevent the droplet spreading. A permanent cylindrical magnet (K&J Magnetics, grade ND42) with a tapered tip was attached to the XYZ linear stage (VT-21, Mikos) to allow the alternation of the field gradient by moving the stage with a 100 nm minimum step in the vertical direction. The process was recorded with a Photron FastCam and Dalsa cameras at 100 fps. Videos were analyzed with VirtualDub (http://www.virtualdub.org) and ImageJ (NIH) software. The magnetic field was calculated numerically by using the FEMM software (http://www.femm.info) (Fig. 1a) and then the numerical results were confirmed by the measurements of the magnetic field at the central axis with a digital teslameter (133-DG GMW Inc.) positioned with the manipulator (VT-21, Mikos) at different distances \( l \) from the magnet (diamonds in Fig. 1f). For further analysis, we approximated the axial component of the magnetic field using the formula \( B = b/l = -0.735/l \) which was proven correct in the range \( 1.7 \text{ mm} < l < 7.1 \text{ mm} \) (the dashed line in Fig. 1f).

**Conclusion**

We studied the behavior of droplets of colloids of nickel nanorods and nanobeads in non-uniform magnetic fields. The droplets form cusps as they do in a uniform magnetic field where this effect is known as the Rosensweig instability. However, in contrast to the uniform field where the entire droplet undergoes deformation, in a non-uniform magnetic field the cusp is localized at the droplet apex where all nanoparticles are collected. When the field is removed, nanorods diffuse away and the cusp disappears. In contrast, nanobeads stay aggregated; finally, the aggregates settle down to the bottom of the drop. The X-ray phase contrast imaging reveals that nanorods in the cusps stay parallel to each other without visible spatial order of their centers of mass. Experiments and scaling theory reveal an interesting universality of the magnetic cusps. It appears that magnetic cusp can be considered as a "frozen magnetic cluster" acting on the drop as a solid object. The contact angle where the part of a droplet free of nanoparticles meets the magnetic cluster is well defined. It is universal for all droplets of different generations. It is equal to \( \beta = 49^\circ \), the famous Taylor angle.44 These experiments and model of cusp formation where the magnetostatic and surface tension forces control the cusp shape show an interesting possibility to align nanorods in a meniscus by applying a magnetic field. Magnetic and electrostatic analogies suggest that a similar ideal ordering can be achieved with the rod-like dipoles subject to a strong electric field. This possibility offers vast opportunities for preordering of carbon nanotubes, nanowires and nanoscrolls prior to spinning them into superstrong and multifunctional fibers.

**Acknowledgements**

The authors are grateful for the financial support of the National Science Foundation through Grant EFRI 0937985, and of the Air Force Office of Scientific Research through Grant FA9550-12-1-0459. We also acknowledge Sigma Xi Grants-in-Aid of Research G20100315153485 and G20100315153500. The use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract no. DE-AC02-06CH11357. We thank Ian Griffiths, Scott Tsai, and Howard Stone for bringing our attention to ref. 48.

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