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DISCUSSIONS

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Field-assisted self-assembly process: general discussion

Yugang Sun, Leonardo Scarabelli, Nicholas Kotov, Moritz Tebbe, Xiao-Min Lin, Ward Brullot, Lucio Isa, Peter Schurtenberger, Helmuth Moehwald, Igor Fedin, Orlin Velev, Damien Faivre, Christopher Sorensen, Régine Perzynski, Munish Chanana, Zhihai Li, Fernando Bresme, Petr Král, Emre Firlar, David Schiffrin, Joao Batista Souza Junior, Andreas Fery, Elena Shevchenko, Ozgur Tarhan, Armand Paul Alivisatos, Sabrina Disch, Rafal Klajn and Suvojit Ghosh

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Petr Král presented some slides on modeling of nanoparticle self-assembly: Realistic modeling of nanoparticle self-assembly necessitates a careful description of all the essential characteristics of the studied systems. In several recently studied systems, we had to perform a detailed analysis of the experimental conditions to understand the important characteristics and realistically capture the observed self-assembly phenomena. I will summarize some of these features:

Self-Assembly of Magnetite Nanocubes into Helical Superstructures:[1] Here, we had to correctly describe all the magnetic and spatial degrees of freedom. The following terms were included: Zeeman coupling, magnetic anisotropy, dipole–dipole coupling, bulk vdW coupling, and effective surface vdW coupling (ligands). Mean-field models can be used, but they need to be carefully parametrized. Frustration of the coupling symmetries leads to the emergence of chirality, which cooperatively propagates through the self-assembling structures.

Chiral Templating of Self-Assembling Nanostructures by Circularly Polarized Light:[2] Here, chiral NPs were able to cooperate and form chiral superstructures. Without precise modeling of the water solvent, acting as a soft cushion between the NPs, the structures would sit face-to-face with each other and the superstructures would not be chiral.

Diffusion and Filtration Properties of Self-Assembled Gold Nanocrystal Membranes:[3] Here, separation properties of NP-membranes were observed. Without careful atomistic modeling, also taking into account the presence of disorder in the NP sizes and densities of the ligands, the pores between NPs would not form or would form without the correct sizes.

Colloidal Nanocube Supercrystals Stabilized by Multipolar Coulombic Coupling:[4] Here, truncation of nanocubes leads to more open superstructures. While we postulated and tested multipolar coupling as the origin of this behavior,

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it is probably the interplay of bulk vdW coupling and overall solvation, given by the type of used ligands and solvents, which is more likely responsible for these phenomena.

Interfacial Localization and Voltage-Tunable Arrays of Charged Nanoparticles:[5] Careful atomistic modeling (in large boxes) of supercharged NPs at the interfaces of different ionic solutions can explain the submergence of these NPs into one of the solvents. It can also capture the coupling of more such NPs and eventually the dependence of the lattice constant on the electric field applied to the interface.

Self-standing Nanoparticle Membranes and Capsules:[6] Some of the less delicate phenomena can be captured by coarse-grained modeling, such as the mechanical properties of the self-assembled NP membranes. We can describe a transition from disordered to highly organized behavior of the NPs during the membrane stretching. Other systems of interest based on ligated NPs have been studied recently, especially in combination with their applications in bio-systems. In such cases, precise atomistic force fields need to be developed to capture all the details associated with coupling of NP ligands and bio-components (drugs, lipids, proteins, DNA, *etc.*) Even the description of NP solvation requires precise force fields.

1 G. Singh, H. Chan, A. Baskin, E. Gelman, N. Repnin, P. Král and R. Klajn, *Science*, 2014, **345**, 1149.
2 J. Yeom, B. Yeom, H. Chan, K. W. Smith, S. Dominguez-Medina, J. H. Bahng, G. Zhao, W.-S. Chang, S.-J. Chang, A. Chuvilin, D. Melnikau, A. L. Rogach, P. Zhang, S. Link, P. Král and N. A. Kotov, *Nat. Mat.*, 2015, **14**, 66.
3 J. He, X.-M. Lin, H. Chan, L. Vuković, P. Král and H. M. Jaeger, Diffusion and Filtration Properties of Self-Assembled Gold Nanocrystal Membranes, *Nano. Lett.*, 2011, **11**, 2430.
4 H. Chan, A. Demortiere, L. Vuković, P. Král and C. Petit, *ACS Nano*, 2012, **6**, 4203.
5 M. K. Bera, H. Chan, D. F. Moyano, H. Yu, S. Tatur, D. Amoanu, W. Bu, V. M. Rotello, M. Meron, P. Král, B. Lin and M. L. Schlossman, *Nano Lett.*, 2014, **14**, 6816.
6 H. Chan and P. Král, *Nanoscale*, 2011, **3**, 1881.

Damien Faivre opened a general discussion of the paper by Rafal Klajn: At high magnetic field, I would expect remagnetization to occur since the energy difference between the hard and easy axis of magnetization is not so high. In this case, you would have both forces acting along the 100 direction and loss of your chiral structure. Have you observed any field dependent pattern?

Rafal Klajn replied: Our self-assembly experiments were performed under relatively low (less than 700 G) applied magnetic fields. We agree that under high fields, reduced magnetocrystalline anisotropy is expected, with both the van der Waals and magnetic interactions favouring the formation of simple one-dimensional filaments.

Leonardo Scarabelli asked: My question regards the possibility of tuning the forces that act on the magnetic building-blocks once the self-assembly is already completed. For example, what would happen if I shine light on magnetic nanocubes functionalized with the azobenzene ligand but assembled as helices (in the dark)? Would they rearrange, or are they frozen in their conformation after drying?

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Rafal Klajn responded: Once the self-assembly of magnetite nanocubes has been completed, and the solvent has evaporated, the particles are "frozen" in the assembled state. Exposing these kinetically trapped assemblies to magnetic fields or light does not affect their structures. It is likely, however, that under conditions of limited particle mobility (*e.g.*, in the presence of solvent vapours), rearrangements of/within the assembled structures could be observed.

Ward Brullot asked: In the presented paper, the authors touch on the notion of homochirality of life on earth. A number of theories on the origin of homochirality have been described, amongst others micro-RNA or circular starlight. The authors suggest that the phenomenon of homochirality might be explained by the induced chirality of iron oxide nanoparticle superstructures. As the balance of forces required for chiral nanoparticle assemblies to form as put forward in the paper is delicate, what is the probability that all these forces were indeed balanced at the time life began?

Rafal Klajn replied: We are not able to comment on the probability of anything occurring "at the time life began".

Orlin Velev opened discussion of the paper by Nicholas Kotov: The assembly of high-surface area electrodes and current collectors from conductive nanoparticles makes a very compelling materials science case. However, the current has to pass through the areas of nanoparticle contact, which are very small in size and could be easily contaminated by thin organic nanolayers. In addition, the high current density in the junctions may lead to thermal degradation. Have any of these been observed as a problem in the practical prototypes you have created?

Nicholas Kotov responded: TEM data in Fig. 5 as well as other studies from our group[1–3] indicate that the nanoparticles at the point of contact recrystallize and form bridges with continuous lattice-to-lattice connectivity. From what we currently know, such contacts cannot be easily contaminated or destroyed by surrounding surfactant molecules. The question about the effect of high current densities is more difficult to answer. I would also anticipate that it might be a problem for high charge–discharge (C–D) rates. We have not observed such degradation for higher-than-typical C–D rates of 1 C. Considering the possibility of making cathodes with C–D rates that are more that two orders of magnitude higher,[4,5] the thermal effects at junctions may not be ignored and should be investigated.

1 Z. Tang, N. A. Kotov and M. Giersig, *Science*, 2002, **297**(5579), 237–240.
2 A. Querejeta-Fernández, J. C. Hernández-Garrido, H, Yang, Y. Zhou, A. Varela, M. Parras, J. J. Calvino-Gámez, J. M. González-Calbet, P. F. Green and N. A. Kotov, *ACS Nano*, 2012, **6**(5), 3800–3812.
3 G. Ma, Y. Zhou, X. Li, K. Sun, S. Liu, J. Hu and N. A. Kotov, *ACS Nano*, 2013, **7**(10), 9010–9018.
4 R. Mo, S. O. Tung, Z. Lei, G. Zhao, K. Sun, N. A. Kotov, *ACS Nano*, 2015, **9**(5), 5009–5017.
5 B. Kang and G. Ceder, *Nature*, 2009, **458**, 190–193.

Orlin Velev continued discussion of the paper by Rafal Klajn: The nanoparticles in your experiment are organised by magnetic field, which can lead to induced and residual magnetic moment. The induced moment will lead to

interactions during the field application, while the residual polarization will cause attraction after the field is turned off. What is the relative extent and strength of these components of the magnetic interactions? Is the residual polarization stronger than the thermal energy of the particles?

Rafal Klajn responded: Indeed, induced magnetic fields may be many times stronger than applied fields, and they are thought to play an important role during self-assembly of magnetic nanocubes in our system. When magnetic field is turned off, however, the magnetic interactions between the particles are negligible (consistent with the superparamagnetic nature of the nanoparticles); however the addition of a solvent (*e.g.* hexane) leads to rapid redissolution of the particles (and disassembly of the helices). In other words, the thermal energy of the particles overcomes the residual polarisation.

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Xiao-Min Lin enquired: Have you measured the magnetic properties of the helical structure of iron oxide nanoparticles? Is there any difference in magnetic properties compared with a flat straight stripe of nanoparticles?

Rafal Klajn replied: We have not yet investigated the magnetic properties of the helical assemblies; therefore we cannot comment on any possible differences between the helical and non-helical filaments. One can expect some differences because within the helices the nanocubes have their body diagonals (*i.e.*, easy axes of magnetisation) aligned roughly parallel to the main axes of the filaments, which is not the case for cubes assembled into one-dimensional stripes. In addition, possibly, collective effects due to the helical structures might contribute to their magnetic properties.

Igor Fedin asked: Fig. 2 shows a portion of a domain of self-assembled helices of identical chirality. Do you have an estimate of domain size? Or of how many domains there are per batch? Have you ever observed multiple domains in the same SEM (or TEM) view? Have you observed a phase boundary between two adjacent domains, where helices are assembled as ...R R R R R R R L L L L L L L...., where R is a right-handed and L is a left-handed helix?

Petr Král responded: This might be a question for Rafal who does the experiments. Yes, domains and their boundaries have been observed (see Fig. 1 below)[1].

1 G. Singh, H. Chan, A. Baskin, E. Gelman, N. Repnin, P. Král, and R. Klajn, Self-Assembly of Magnetite Nanocubes into Helical Superstructures, *Science*, 2014, **345**, 1149.

Rafal Klajn also responded: The average domain size could be correlated with the rate of solvent evaporation, and it could be clearly observed by TEM/SEM imaging. Under carefully controlled conditions, the domains of helices having the same handedness as large as 1 mm^2 could be obtained. We could readily image two or more domains at once; see, for example, Fig. 2H in ref. 1, which shows a phase boundary between right- and left-handed helices.

1 G. Singh, H. Chan, A. Baskin, E. Gelman, N. Repnin, P. Král and R. Klajn, *Science*, 2014, **345**, 1149–1153.

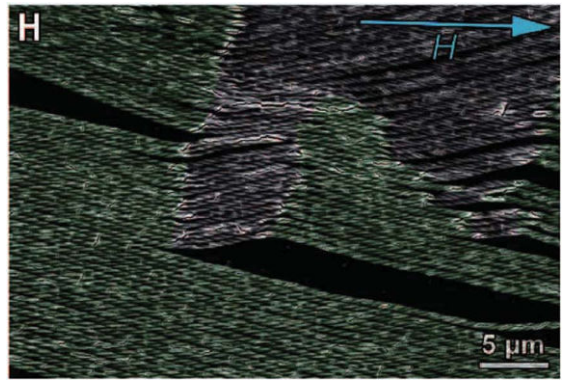


Fig. 1

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Zhihai Li resumed discussion of the paper by Nicholas Kotov: In Fig. 2, showing the electrochemical reduction of Cu ions, the electrochemical potential value of reduction was indicated, but what was the reference electrode?

Nicholas Kotov replied: We typically use a silver/silver chloride electrode for CV measurements using Epsilon electrochemical workstation from Bioanalytical Systems, Inc.

Zhihai Li asked: In Fig. 2c, how do you treat the substrate before reductive deposition of the Cu ion? Did you add an additive, or carry out any additional treatment, to make such well-defined surface nanocrystals?

Nicholas Kotov responded: Thanks a lot for this question because we also considered it in the past. Some special additives may indeed be used for electrodeposition. However, no special additives besides the composition of the electrolytic bath solutions were used. The approximate diameter of copper dendrites in Fig. 2c is 200–300 nm.

Andreas Fery returned to discussion of the paper by Rafal Klajn: Is the idea of adding plasmonic nanoparticles to introduce optical functionality, and, if yes, can larger particles be attached?

Rafal Klajn replied: We investigated the self-assembly properties of various types of superparamagnetic nanoparticles, including Ag-Fe_3O_4 heterodimers. We observed the formation of well-defined helices despite the presence of (diamagnetic) silver domains as large as 10 nm. We expect that larger Ag domains would also be possible, if the dimensions of the superparamagnetic domain are proportionally larger.

Andreas Fery asked: Can catalytically active substances be infiltrated into pores of the helical arrangements ? Can they act as chiral templates for synthesis ?

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Rafal Klajn answered: Various achiral molecular catalysts could readily be deposited on top of self-assembled helices; perhaps they could also infiltrate into the pores between the nanocubes. The resulting materials could potentially act as asymmetric catalysts.

Yugang Sun continued discussion of the paper by Nicholas Kotov: The low-current field assisted assembly has been demonstrated to be capable of assembling Cu nanoparticles into beautiful 3D mesoscopic structures. I believe that this strategy could be extended to assemble other nanoparticles into similar mesoscopic structures. Is it possible to assemble two (or more than two) different types of nanoparticles simultaneously to form hybrid mesoscopic 3D structures? Probably different 3D structures can be formed through the low-current field assisted assembly when the nanoparticles are changed, is this true? If so, what condition of the nanoparticles represents the most important parameter to determine their assembly behavior?

Nicholas Kotov answered: I agree that this assembly behavior is not exclusive to copper nanoparticles. It can be extended to other particles as well, with expectations of a similar "squeezing out" of the surfactant layer. Charge and zeta-potential of the nanoparticles appear to me to be the most important parameter determining their behavior in electrophoretic deposition.

Yugang Sun said: Following my previous question, when two different components are mixed or co-crystallized, they tend to phase separate to lower the overall system energy. Phase separation may also happen when the low-current field assisted assembly is used to assembly binary (or ternary) nanoparticles. According to your intensive experience and understanding in this assembly technique, what we can do to avoid the possible phase separation?

Nicholas Kotov answered: The electrophoretic assembly of binary mixtures of nanoparticles is definitely possible. I would expect that conditions of the field-driven deposition can be varied to obtain both phase separated and “alloyed” systems. None of these have been demonstrated yet and this will be an interesting direction of research.

David Schiffrin asked: The use of metal nanoparticles for the preparation of electrical contacts instead of classical electroplating methods is an interesting idea, since in some cases it might replace classical electrodeposition methods. The physical separation of the formation of metal precursors from the actual formation of contacts can be advantageous, since it opens up the possibility of forming nanoalloys prior to their incorporation on contacts, thus avoiding the complexities of wet electroplating chemistry. It has been asked during the discussion of this paper that the CTAB stabilising ligand would be detrimental to the electrical contact between metal particles. The high negative potential applied to achieve the proposed electrophoretic deposition would most likely result in desorption of the adsorbed CTAB. If the proposed mechanism of electrophoretic deposition is correct, it is difficult to understand why dendrite formation is observed (Fig. 5A), since no copper is present in solution and no Cu^{++} ions can be incorporated from the Pt electrode employed as the anode. Given that the

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presence of dendrites is considered to be an important feature of the proposed contact fabrication method, an explanation of how these are formed under the conditions employed is required.

Nicholas Kotov replied: I agree that desorption of CTAB is facilitated by the applied potential. Dendrites form in this system due to the tendency of nanoparticles to self-assemble into chains. Linear assemblies of nanoparticles were observed in the past both for semiconductor[1,2] and metallic nanoparticles.[3] Interestingly, such self-organization patterns persist both in the liquid and the solid state, as indicated in the relatively recent study in ref. 4. So the dendritic appearance of the electrodeposited or, to be more exact, electro-assembled films is the reflection of this feature of the nanoparticles. Notably, microscale particles often form films with much smaller porosity and even with a closely packed opal structure[5] under similar conditions of electrodeposition. From this, one can infer that the assembly behaviors of microscale particles and nanoscale particles in electrical field differ markedly. These differences are significant from both the academic and technological perspectives.

1 Z. Tang, N. A. Kotov and M. Giersig, *Science*, 2002, **297**(5579), 237–240.
2 Y. Ming, K. Sun and N. A. Kotov, *J. Am. Chem. Soc.*, 2010, **132**(6), 1860–1872.
3 Y. Sun, B. Mayers, T. Herricks and Y. Xia, *Nano Letters*, 2003, **3**, 955–960.
4 Y. Kim, J. Zhu, B. Yeom, M. Di Prima, X. Su, J.-G. Kim, S.-J. Yoo, C. Uher and N. A. Kotov, *Nature*, 2013, **500**, 59–64.
5 A. L. Rogach, *Chem. Mater.*, 2000, **12**, 2721–2726.

Munish Chanana resumed general discussion of the paper by Rafal Klajn: Dear Rafal Klajn, you mentioned in your presentation that you cannot control left or right handedness in your assemblies. You also mentioned that you assume or know that the left or right handedness comes from the handedness of the very first structures that are built during the process. So my questions is, is it possible to introduce a desired handedness into the system, by introducing a piece of an assembled structure of known handedness from a previous assembly into the next assembly, thus controlling the final handedness of your system?

Rafal Klajn replied: This question raises the intriguing possibility that seeded growth occurs during nanoparticle self-assembly. Apparently, arrays of filaments oriented in a particular direction with respect to the applied magnetic field during the self-assembly process might induce the formation having helices of a desired handedness.

Helmuth Moehwald addressed all the attendees: A remark on chiral separation. Certain minerals have chiral surfaces, and these have been shown to adsorb oligonucleotides *enantio*-selectively. This could also be used to select chiral structures according to chirality.

Armand Paul Alivisatos answered: I very much agree. I think that is a very promising research direction.

Nicholas Kotov also answered: Interparticle interactions of nanoparticles coated with a layer of chiral stabilizers or those having chiral inorganic phases in

the nanoscale cores can be enhanced/facilitated tremendously *via* collective interactions in nanoparticle assemblies. This can indeed be very useful for chiral separations.

Christopher Sorensen resumed discussion of the paper by Rafal Klajn: You stated that both left and right handed structures nucleated at random. Have you considered breaking the symmetry by including a rotating magnetic field along with the static field?

Rafal Klajn responded: We agree that complex magnetic fields could potentially give rise to the preferential formation of helices having a given handedness. We are also considering an approach based on modifying the surfaces of magnetite nanocubes with monolayers of chiral ligands, and using these functionalized particles as the building blocks.

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Moritz Tebbe remarked: Can these helical superstructures consisting of magnetic nanoparticles be rotated, applying a rather weak external magnetic field to use them as nano/micro propellers and eventually move them within the solution?

Rafal Klajn responded: Adding a good solvent (*e.g.*, hexane) to arrays of helices assembled on solid substrates induces the particles to dissolve and the helices to disassemble. However, one can envision several possible ways to obtain stable dispersions of the helical nanostructures. For example, cubes comprising the helices could be covalently crosslinked upon the addition of compounds such as α,ω-dicarboxylic acids. Alternatively, thermal treatment of self-assembled helices on solid substrates should result in ligand desorption and coalescence of neighboring nanocubes yielding continuous filaments in which the helical features might be retained.

David Schiffrin communicated to Nicholas Kotov: The impedance results (Fig. 7) refer to a whole cell, while the equivalent circuit employed for the analysis refers only to that of one electrode, whereas in the cell investigated the two electrodes forming it are in series. How did you deconvolute these results to obtain data pertaining only to the new Cu–graphite composite investigated (Table 3)?

Nicholas Kotov communicated in reply: This is a good point and indeed deserves clarification. As mentioned in section 4.6 Electrochemical Measurements, EIS spectra were obtained using lithium foil as both the counter and reference electrodes, and a graphite-pasted Cu electrode as the working electrode. In this cell, the impedance at the lithium metal electrolyte interface is much smaller than that at the Cu electrode–electrolyte interface and can be neglected in calculations. After the meeting we tested this assumption and it was indeed correct; the same assumption was used in other studies exemplified by those referred to in ref. 1.

1 E. Frackowiak and F. Beguin, *Carbon*, 2001, **39**, 937.

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Régine Perzynski opened the discussion of the paper by Orlin Velev: Electro-rheological and magneto-rheological fluids are based on particles of several tens of microns inside a liquid, and the usual tools of mechanics can describe their behaviour.

When getting down to dispersions of particles of few tens of nanometers in size, Brownian agitation kT becomes of prevailing importance and cannot be forgotten in the (then thermodynamic) description of the stability of such systems. The present mixture of 20 nm ferrite particles, coated with 12-hydroxysteric acid (as shown in Fig. 1d), dispersed in water clearly comes into this category, also named ferrofluids or magnetic fluids. In such systems, depending on the balance of attraction and repulsion with respect to kT, various states of the system can be obtained.[1,2]

- Homogeneous dispersion (your observations reject this).

- Irreversible aggregation in the first minimum (your observations are not in favor of this either, to my understanding).

- A phase separation in a very dilute phase, co-existing either with liquid droplets, which are concentrated in NPs (as in ref. 3 for example), or co-existing with gel-like or solid-like aggregates (see ref. 1).

Your description in terms of liquid bridges between NPs recalls the description of the liquid concentrated phase of ref. 3, however your aggregates are not spherical in zero field (neither before applying the field (Fig. 1a) nor after (Fig. 1c)) and seems to behave elastically (solid-like) and not as a liquid as in ref. 4 and 5, for example, where strange liquid shapes are obtained in a rotating field with such liquid droplets. However, the shapes of Fig. 4a–c adopted by the aggregates under the rotating field recall some of ref. 5 (see the two dynamic pictures below, extracted from ref. 5).

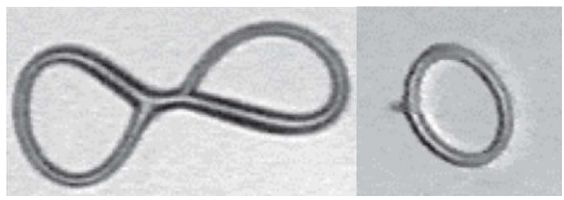


Fig. 2 Shapes adopted by a (few 10 μm in diameter) droplet of concentrated ferrofluid (in a phase separated system) under a 2D rotating magnetic field (from ref. 5 – Copyright *Magnetohydrodynamics*, Latvijas universitāte, Fizikas institūts, 2000).

Moreover, frequently (ref. 6 and 7), such a liquid–liquid phase separation can be impeded by a "gel line", leading to concentrated aggregates, which are solid-like and are made either of a soft gel or of a glass, depending on the coating of the dispersed objects and on the balance of the interactions. If these objects are magnetic, it then leads under-field to elongated aggregates, persisting in zero-field in configurations closely similar to those of Fig. 1c and adopting under rotating field auto-organizations also similar to those of Fig. 4 e–g.

My question is: could you comment on the colloidal state of your system in this thermodynamical framework, and not only in the (nice) mechanical framework adopted in the paper?

1 F. Cousin, E. Dubois and V. Cabuil, Tuning the interactions of a magnetic colloidal suspension, *Phys. Rev. E*, 2003, **68**, 021405 1–9.
2 E. Dubois, V. Cabuil, F. Boué and R. Perzynski, Structural analogy between aqueous and oily magnetic fluids, *J. Chem. Phys.*, 1999, **111**, 7147–7160.
3 O. Sandre, J. Browaeys, R. Perzynski, J.-C. Bacri, V. Cabuil and R. E. Rosenweig, Assembly of microscopic highly magnetic droplets: Magnetic alignment versus viscous drag, *Phys. Rev. E*, 1999, 59, 1736–1746.
4 J. C. Bacri, A. Cebers and R. Perzynski, Behaviour of a magnetic fluid microdrop in a rotating magnetic field, *Phys. Rev. Lett.*, 1994, **72**, 2705–2708.
5 E. Janiaud, F. Elias, J.-C. Bacri, V. Cabuil and R. Perzynski, Spinning ferrofluid microscopic droplets, *Magnetohydrodynamics*, 2000, **36**, 365–368.
6 F. Cardinaux, T. Gibaud, A. Stradner and P. Schurtenberger, Interplay between spinodal decomposition and glass formation in proteins exhibiting short-range attractions, *Phys. Rev. Lett.*, 2007, 99, 118301.
7 H. Verduin and J. K. G. Dhont, Phase diagram of a model adhesive hard-sphere dispersion, *J. Coll. Interface Sci.*, 1995, **172**, 425–437.

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Orlin Velev replied: The question relates to comparing the properties of the filaments bound by nanocapillarity to the ones of common ferrofluids and the framework of conventional colloidal interactions between nanoparticles. This is an important question and both of these correlations are relevant. Our system displays some properties that are present either in ferrofluids or dispersed NPs in liquid. In most of the ferrofluid systems the NPs are dispersed in an oil-type phase. In most conventional colloidal studies the NPs are dispersed in water and are stabilized electrostatically or sterically. In our system, we have both an oil phase (coating the particles) and a water phase (where they are all dispersed). The interactions present in ferrofluids and water are present in the background, but the new and overarching interactions are based on the O/W interfaces around the liquid bridges of the NPs. This requires a precise balance of the components (*e.g.* if we add more oily fatty acid phase we will end up with ferrofluid-like droplets). Understanding the precise delicate interplay of all these interactions in the context of the capillarity and magnetophoresis present in the system is a task for our future research.

Lucio Isa asked: The particle chains linked by liquid–lipid bridges have a pronounced elongated shape. If the linkage is provided by capillary bridges, why don't they drive the collapse of the chains into spherical droplets when the field is turned off?

Orlin Velev replied: In principle, the capillary forces will indeed be minimized if the liquid-coated nanoparticles form large "droplet"-like assemblies with multiple liquid bridges between the particles (it is also possible to form a completely single liquid phase droplet depending on the amount of fatty acid around the particles in the beginning). However, we do not observe the formation of such structures or a significant degree of spontaneous nanoparticle re-arrangement in the filaments after their assembly within the timescales of the experiment (hours). The likely reason for this is the physical jamming of the particles and the high energy of the bridging, which is not easily overcome by thermal fluctuations. Thus relaxation times for their rearrangement are likely very long. In effect, the filaments are metastable structures, but so are an enormous number of other colloidal and nanoscale systems.

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Lucio Isa commented: It was very nicely demonstrated that under oscillatory fields the chains can rearrange and when two ends meet, they merge, snapping into contact. Could it be possible that thermal fluctuations also bring different parts of the chains into contact, leading to coalescence over time?

Orlin Velev replied: As mentioned already, this is likely to be the case if we let the chains undulate and relax over long time periods. We observe occasional snapping of the thermally fluctuating filaments end-to-end or to other nearby filaments. However, this process is slow. We can rapidly directionally attach the chains to each other, or close them, by dynamic magnetic fields. We do not observe further coarsening of the structures after end-to-end attachment, as the internal thermal reconfiguration of the structures likely occurs on much slower time scales.

Nicholas Kotov asked: Can the collapse of the chains into droplets be prevented due to electrostatic repulsion of the particles?

Orlin Velev answered: I believe that this question addresses a key aspect of our system, as the electrostatic repulsion between the nanoparticles in water dispersion is likely key in keeping them in a (quasi)stable configuration. The electrostatic repulsion prevents the liquid-coated particles from immediate aggregation upon contact. Thus, we need the additional force applied by the magnetic fields in order to overcome the repulsive electrostatic barrier and have the liquid coated surfaces stay in contact. The directional assembly driven by the magnetophoretic force leads to the formation of the filaments, rather than randomly directed droplet-like aggregates, which would be the case had there not been electrostatic repulsion. The role of the electrostatic repulsion in stabilizing the assembled filaments is less clear at this point, but obviously it is an important component of the assembly process.

Elena Shevchenko queried: Does the arrangement of your magnetic chains change if you apply a magnetic field with different direction? It looks like your chains have great memory.

Orlin Velev replied: Indeed, the magnetic filaments (we use this term to distinguish from single-line chains) have some residual magnetic polarization and follow the orientation of the field. While the particles are generally superparamagnetic, their massive assemblies have enough residual polarization to follow the field. Interesting structures can be formed depending on the field direction and rotation velocity. The field-driven orientation is also the factor that plays a role in self-repair of the gel. If the repairing field is at a angle, the chains would also re-connect along the direction of the field.

Peter Schurtenberger remarked: I would like to return to the previously raised question about the stability of these flexible chains after the field has been turned off, and whether this could be due to the effect of the present charges on the particles. There are in fact a number of systems where the presence of a short range attraction in combination with a more long-range repulsion leads to the formation of equilibrium clusters. Depending upon the balance and the range of

the repulsive contribution, these clusters can either be globular or more anisotropic.[1,2] Such a mechanism could also be responsible for the long-term stability of the chains you describe, despite the presence of a short range capillary attraction that would favor the formation of globules. One way to test this hypothesis would be the addition of different amounts of salt in order to screen electrostatic repulsions and shift the balance towards the capillary attraction.

1 A. Stradner, H. Sedgwick, F. Cardinaux, W. C. K. Poon, S. U. Egelhaaf, P. Schurtenberger, *Nature*, 2004, **432**, 492–495.
2 F. Cardinaux, A. Stradner, P. Schurtenberger, F. Sciortino and E. Zaccarelli, *Eur. Phys. Lett*, 2007, **77**, 48004.

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Orlin Velev answered: Thank you for pointing out these arguments, which are fully consistent with our observations and interpretation of the data. This also addresses the comment of one of the other delegates regarding the lack of slow rearrangement of the particles, which as a matter of fact we do not observe during the experiments. We will seek to confirm the effect of electrostatics, though an experiment with varying electrolyte concentration is somewhat complicated in our system where the fatty acid is in the form of a salt and thus contributes a lot of salt ions to the system, as well as introducing a pH-dependence of the electrolyte. We may attempt an experiment with added electrolyte and compare it with the present filament assembly and stability pattern.

Petr Král opened the discussion of the paper by Suvojit Ghosh: Self-assembly of superparamagnetic nanoparticles was discussed. Is it possible to design a material that transitions from paramagnetic to ferromagnetic, depending on ligand length/size of particles?

Suvojit Ghosh replied: Such material design possibilities, emerging from the influence of the organization of nanoparticles on the bulk properties of a material, form the motivation for this study. For instance, by selecting an appropriate particle size, a low ligand length will yield ferromagnetism whereas a high ligand length will lead to superparamagnetism.

Emre Firlar returned to the discussion of the paper by Orlin Velev: You showed cryo-TEM images. I am wondering about their sample preparation methods. Did you use immersion in liquid nitrogen, cryoplunging, HPF or other methods? Did you also have a chance to investigate the effect of dose on the bridge formation around the nanoparticles? Could you also please give information about the dose you used during cryo imaging?

Orlin Velev replied: The cryo-TEM observations of the samples were performed on a JEOL JEM-1230 TEM operating at 80 kV. The nanoparticle–lipid samples were prepared by common flash-freezing in liquid. The images were recorded under low dose conditions, without any visible deterioration of the samples.

Helmuth Moehwald resumed discussion of the paper by Suvojit Ghosh: In the manuscript the authors use an Arrhenius type equation to describe reorientation dynamics, but then need to assume a frequency factor varying by 3 orders of magnitude. At the end they find a phenomenological way out, where the

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frequency depends on a term $(V - V_0)$. There they have a problem, in that there is no model, but only a phenomenological equation. However, one can find this dependence one can find in classical diffusion models in liquids (Cohen and Turnbull), and in glasses, polymers, biomembranes, *etc*. These run under free volume models. Did the authors consider this aspect?

Suvojit Ghosh responded: We did not consider this aspect during the study, but the question raises an intriguing point. There is no direct physical analogy between the concept of free volume (*e.g.* as defined in ref. 1) and the V_0 determined here from the computational data in Fig. 5. However, considering that V_0 emerges from reorganization of interacting spins, a similar analysis can be foreseen. We will study this closely in the future.

1 J. O. Hirschfelder, D. P. Stevenson and H. Eyring, *J. Chem. Phys.*, 1937, **5**, 896.

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Nicholas Kotov resumed discussion of the paper by Orlin D. Velev: I was thinking about the frequency effect on the flexibility of chains. What do you think about the possibility of establishing the forces between the NPs by studying the effect of frequency of a switching magnetic field? The point when the frequency of magnetic field switching is so high that it is no longer affecting the shape of the chains might be particularly informative.

Orlin Velev responded: This is an excellent idea that we are presently investigating. This is done by periodically switching the direction of the field after the filaments are assembled. The timed switching of the field direction leads to the formation of various shapes of the filaments that snap on contact – circles, infinity, "hearts" and so on. The shape of these structures depends on the speed of switching of the field direction (equivalent to frequency). We plan on analyzing these results on the basis of the theoretical framework established earlier by A. Gast and S. L. Biswal[1,2] for the case of magnetic nanoparticle chains bound by DNA. While these experiments would yield valuable information, the analysis of the data is non-trivial and we expect to be able to report these ongoing studies in the future.

1 S. L. Biswal and A. P. Gast, Rotational dynamics of semiflexible paramagnetic particle chains, *Phys. Rev. E. Stat. Nonlin. Soft Matter Phys.*, 2004, **69**, 041406.
2 D. Li, S. Banon, and S. L. Biswal, Bending dynamics of DNA-linked colloidal particle chains, *Soft Matter*, 2010, **6**, 4197–4204.

Petr Král asked: Motility should be prevented at a small scale due to low Reynolds numbers, have you thought about this? With small, *e.g.* 10 nm particles, do they still have motility?

Orlin Velev responded: In this work we observe the dynamics of micron-sized chains, which are much larger than single NPs and readily respond to relatively weak magnetic fields (not least because they are very flexible and ductile). However, we have earlier observed a number of effects of electric-field driven nanoparticle concentration and aggregation, as in our papers in Science[1] and Langmuir.[2] In general, I believe that 10 nm NPs readily exhibit dielectrophoretic (DEP) and magnetophoretic (MEP) motility. The reason for this is that the

phoretic forces are rather strong, and the laminar nature of the flows is not enough to suppress them as in the case of "active" self-motile nanoparticles.

1 K. D. Hermanson, S. O. Lumsdon, J. P. Williams, E. W. Kaler, and O. D. Velev, Dielectrophoretic assembly of electrically functional microwires from nanoparticle suspensions, *Science*, 2001, **294**, 1082–1086.
2 K. H. Bhatt and O. D. Velev, Control and modeling of the dielectrophoretic assembly of on-chip nanoparticle wires, *Langmuir*, 2004, **20**, 467–476.

Ozgur Tarhan questioned: Have you identified the factors influencing the rate of self-assembly of microfilaments? Temperature? Fatty acid chain length? Or any other parameter?

Orlin Velev responded: This question is key to understanding the assembly phenomenon and is closely related to the important issue of fatty acid fluidity. We have investigated both of these effects and have proven that the assembly occurs only in the cases when the lipid is in the liquid state (and thus can form the bridges between the particles). These results will be analyzed and reported in a separate publication.

Fernando Bresme opened communication on the paper by Sabrina Disch:† This is an interesting investigation of magnetic particle assembly. In Fig. 2a the authors show that in the absence of a field the sample features weak correlations. I wonder whether stronger correlations may be present, perhaps in the bulk, connected to the formation of liquid crystal phases? The formation of these phases is favoured by excluded volume effects and particle anisotropy.[1] Could the formation of these structures be present in the bulk regions? Or is it simply that the thermodynamic conditions (packing fraction) do not favour LC phases in this case?

1 J. T. Brown, M. P. Allen, E. M. del Río and E. de Miguel, *Phys. Rev. E*, 1998, **57**, 6685.

Sabrina Disch communicated in reply: The formation of nematic liquid crystal phases as induced by van der Waals interactions or excluded volume effects is indeed an important aspect for spindle-type nanoparticles. We know that when the particles are dispersed in water in the concentration range 6–10 vol%, the formation of a nematic phase is observed even without application of an orienting magnetic field. Considering the process of evaporation-induced particle deposition that occurs under steady increase of the particle concentration towards an entirely dried sample, the formation of nematic domains in the course of this process is likely. However, we observe that the structural correlation length of such transient nematic domains manifested in a limited number of aligned particles in our sample (Fig. 2a) seems to be very short, corresponding to locally restricted collinear orientation of the nanoparticles. In consequence, the samples prepared by deposition without an applied field are macroscopically isotropic, as confirmed by the directionally dependent magnetization measurements shown in Fig. 5a. If a magnetic field is applied during deposition of the sample, the field-

† Sabrina Disch's paper was not presented at the meeting. Questions were submitted to the author afterwards.

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induced orientation of the spindles leads to a significant increase of the nematic domain size, resulting in the directionally anisotropic assemblies discussed in our contribution.

Fernando Bresme communicated to Suvojit Ghosh: Could you comment on the applicability of equation 11? These type of equations are derived, often, for the case of an isolated particle. How general is this equation, does it apply to the more general case of a system of interacting particles?

Suvojit Ghosh communicated in reply: Equation 11 is derived from the Néel–Arrhenius relation of equation 1 by calculating an appropriate value of the "average" potential barrier. Strictly speaking, an Arrhenius type equation describes the frequency of oscillations in a system that experiences an unique potential barrier E_b separating two equilibria, and the barrier is independent of the path traversed between the two equilibria. This is true for an isolated particle (assuming uniaxial anisotropy) whose energy map is described in equation 2 . It is not true for an interacting system of particles, described by equation 5, as the potential barrier is path-dependent and thus does not have a unique value. As a result, our first task was to determine if the Arrhenius type equation can be applied by calculating an "average" potential barrier. This is established in Fig. 2, where a system of two particles is seen to have its spin reversal frequency decay exponentially with $1/T$. It is further confirmed in Fig. 5, where the spin reversal frequency in an interacting system of up to 5 particles decays exponentially with the volume, *i.e.*, E_b.

Joao Batista Souza Junior communicated to Sabrina Disch: The spindle-like hematite nanoparticles were electrostatically stabilized with citric acid and tetramethylammonium hydroxide. The self-assembled nanoparticles in the static magnetic field showed a collinear particle orientation, attributed to steric effects such as van der Waals interactions between the particles or excluded volume effects. My questions are, how stable are these self-assembled films in the silicon substrate? And how long could you preserve these films keeping their magnetic properties? Because the interaction between particles and between particles and substrate are supposedly weak.

Sabrina Disch communicated in reply: As the self-assembled samples are subject to a magnetic field until the organization process is finished, *i.e.* until the samples are completely dried, we do not observe any structural instability of the samples after deposition. We have verified this by SEM and magnetization measurements that were repeated a few months after the deposition process. The long-term stability of the finally dried assemblies is not a result of van der Waals or dipolar interactions between the particles, but rather due to the particle coating and adhesion of the particles as in hard agglomerates.

Helmuth Moehwald communicated: As the tips of the spindles appear to be given by aggregation kinetics, do they round off with time or temperature?

Sabrina Disch communicated in reply: We have not investigated the ageing processes in these particles in detail. DLS measurements carried out more than a

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year after synthesis have not shown any significant changes in the diffusion constants. We thus conclude that – with the sensitivity of DLS – the particles are stable over years. After thermal annealing, we do observe some limited rounding of the tips, whereas the overall shape stays unchanged.

Helmuth Moehwald communicated: How sensitive is SAXS with respect to the aggregate shape? Taken to an extreme, how different would the curve in Fig. 1a look for a sphere?

Sabrina Disch communicated in reply: For perfectly monodisperse samples, SAXS is highly sensitive to the aggregate shape, as the measured particle form factor is directly related to the radial electron density distribution in the particles. Comparing the extreme example of spheres and elongated particles such as a spindles, the radial electron density distribution of the latter extends to significantly larger real space distances, which is expressed in the form factor by increased smearing of the form factor minima as well as a steeper slope in the lower Q-range. For a real sample, however, the particle shape will be difficult to deduce from SAXS measurements without additional information (*e.g.* from TEM or SEM), in particular if the particle size distribution is large. A large particle size distribution (such as $\sigma_{\log} = 15\%$ in our samples) leads to a strong smearing of the form factor minima, which decreases the shape-sensitivity of the technique. For this reason, we did not extract structural information from the SAXS data shown in Fig. 1a. Instead, we decided to simulate the particle form factor based on the structural information gained from SEM. Comparison with the experimental SAXS data confirms the particle size and size distribution determined by SEM (for a relatively small amount of particles of $n = 100$) for the large sample statistics accessible by scattering techniques.

Christopher Sorensen communicated: You have applied fields on the order of a few tens of milli-tesla during the drying process that lead to the assemblies pictured in Fig. 3. What is the magnetic moment of these nanospindles and hence the magnetic field alignment energy? How does this alignment energy compare to the thermal energy, kT?

Sabrina Disch communicated in reply: A comparison of thermal energy and Zeeman energy of the system is indeed important in order to quantify the impact of the magnetic field on the orientation distribution of the spindles in solution. After these have already been discussed for a magnetic field of 20 mT (applied for deposition in a rotating magnetic field, section 3.3), I am glad to complement the quantitative discussion for the case of a static magnetic field of 38 mT: The moment of the nanospindles has been determined as $\mu = 1.19(2) \times 10^{-18}$ J T^{-1}. The magnetic field alignment energy is derived as $E = \mu\mu_0 H = 4.52(8) \times 10^{-20}$ J. Comparing this energy with the thermal energy at 300 K of $k_B T = 4.14 \times 10^{-21}$ J, we obtain a Langevin parameter $\xi = \mu\mu_0 H/k_B T = 10.9(2)$, illustrating that the magnetic field alignment energy indeed significantly outbalances the thermal energy. The average orientation of the particle moment with respect to the inducing magnetic field is derived from the Langevin parameter by $\langle\psi\rangle = \arccos(\mathscr{L}(\xi)) \sim 24°$.

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At this point I would like to take the opportunity to correct a typographical error in section 3.3, when discussing the average orientation of the particle moment for an applied field of 20 mT (page 10, line 4 in the manuscript). It is stated "This corresponds to an average orientation of the particle moment with respect to the inducing magnetic field of $\langle\psi\rangle = \arccos(\mathscr{L}(\xi)) \sim 40^\circ$." The value of 40° is incorrect; this should correctly be 34°.

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