



# ICMF23 | 16th International Conference on Magnetic Fluids

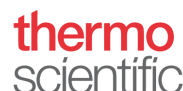
Granada (Spain), 12-16 June 2023



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DE GRANADA

## BOOK OF ABSTRACTS

Edited by Ana Belén Bonhome Espinosa and Laura Rodríguez Arco





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# PROGRAMME

MONDAY JUNE 12

15:00	OPENING CEREMONY (Aula Magna)
15:30	Chair: <u>Modesto T. López López</u>
	PL-1. PLENARY LECTURE: <u>Ladislau Vékás</u> <i>Ferrofluids and ferrofluid driven manufacturing of new materials: advanced characterization and applications</i>
16:10	FSP&FHD-OP-1. Oral - <u>Guillaume Ricard</u> <i>Transition from wave turbulence to acousticlike shock wave regime</i>
16:25	FSP&FHD-OP-2. Oral - <u>Carlo Rigoni</u> <i>Ferrofluidic aqueous two-phase system with ultralow interfacial tension and micro-pattern formation</i>
16:40	FSP&FHD-OP-3. Oral - <u>Jaakko Timonen</u> <i>Electrically Controllable Ferrofluids</i>
16:55	COFFEE BREAK (Main foyer)
17:20	Chair: <u>John Philip</u>
	KNL-1. KEYNOTE LECTURE: <u>Antonio Martins Figueiredo Neto</u> <i>Nonlinear optical properties of magnetic fluids: from single particle to the collective behavior</i>
17:45	EA-OP-1. Oral - <u>Takuya Kuwahara</u> <i>Ionic wind generation from magnetic fluid in various configurations</i>
18:00	EA-OP-2. Oral - <u>Álvaro Gallo Cordova</u> <i>Iron Oxide and Metal Ferrite Nanocatalysts: Insights into the Generation of Free Radicals</i>
18:15	EA-OP-3. Oral - <u>Sawako Nakamae</u> <i>Multifunctional Magnetic Nanocolloids for Hybrid Solar-Thermoelectric Energy Harvesting</i>
18:30	Chair: <u>Kinnari Parekh</u>
	HMT-OP-1. Oral - <u>Mikhail S. Krakov</u> <i>Instability of the miscible magnetic/nonmagnetic fluids flow interface</i>
18:45	HMT-OP-2. Oral - <u>Zhongwu Rong</u> <i>Investigation of Heat Transfer Characteristics of the Self Driven Temperature-Sensitive Magnetic Fluid through a Nonmagnetic Porous in a Circular Tube</i>
19:00	HMT-OP-3. Oral - <u>Huei Chu Weng</u> <i>Experimental investigation on magnetic fluid pool boiling heat transfer on hydrophilic surface</i>
19:15	WELCOME COCKTAIL (Garden of the Faculty of Science)

## TUESDAY JUNE 13 – MORNING SESSIONS

9:00	Chair: <u>Annette M. Schmidt</u>
	<b>PL-2. PLENARY LECTURE: <u>María del Puerto Morales</u></b> <i>Developing efficient processes towards safe magnetic nanoparticles for biomedicine, environmental remediation and catalysis</i>
9:40	<b>LSA-OP-1. Oral - <u>Jean-Michel Siauge</u></b> <i>Synthesis, Characterization and Cellular Internalization of Anisotropic Magnetic Nanoparticles</i>
9:55	<b>LSA-OP-2. Oral - <u>María Salvador</u></b> <i>Magnetic Nanoclusters to Increase the Sensitivity of a Lateral Flow Immunoassay to detect Pneumococcal Pneumonia</i>
10:10	<b>LSA-OP-3. Oral - <u>Tamara Pozo Gualda</u></b> <i>Combined effect of chemotherapy and photothermia based on the use of biomimetic magnetic nanoparticles functionalized with a ChoKa1 inhibitor</i>
10:25	<b>LSA-OP-4. Oral - <u>Oliver Reisen</u></b> <i>Temperature-responsive magnetic nano drug carriers for efficient treatment of pancreatic cancer</i>
10:40	<b>COFFEE BREAK</b> (Main foyer)
11:05	Chair: <u>Orlin Velev</u>
	<b>KNL-2. KEYNOTE LECTURE: <u>Christine Ménager</u></b> <i>How magnetic nanoparticles can reach the cytosol?</i>
11:30	<b>LSA-OP-5. Oral - <u>Erzsébet Illés</u></b> <i>Biocompatible folate targeted cobalt ferrite nanoparticles for magnetic hyperthermia</i>
11:45	<b>LSA-OP-6. Oral - <u>Veronica Salgueiriño</u></b> <i>Taking advantage of the magnetic functionality of nanostructures for induced movement</i>
12:00	<b>LSA-OP-7. Oral - <u>Claudia Lozano Pedraza</u></b> <i>Optical or magnetic activation of iron oxide nanoparticles inside cells? The question behind thermal losses in biological environments</i>
12:15	<b>LSA-OP-8. Oral - <u>Carlos Frade González</u></b> <i>Targetable thermomagnetophoretic nanopump for controlled release of biomolecules</i>
12:30	<b>LSA-OP-9. Oral - <u>Clara Marquina</u></b> <i>Graphene-coated Fe nanoparticle suspensions for Safe and Steady Drug Delivery</i>
12:45	<b>LUNCH</b> (Main foyer)

## TUESDAY JUNE 13 – AFTERNOON SESSIONS

14:15	Chair: <b>Christine Ménager</b>
	<b>KNL-3. KEYNOTE LECTURE: Annette M. Schmidt</b> <i>Universality in Ferronematic Liquids: Polymer-mediated Stabilization of Magnetic Nanodopants of Different Size and Shape in Liquid Crystal Phases</i>
14:40	<b>LSA-OP-10. Oral - Danny Villanueva</b> <i>Magnetic hyperthermia of M. blakemorei</i>
14:55	<b>LSA-OP-11. Oral - Guillermo Iglesias</b> <i>Study of cellular internalization of biomimetic nanoparticles in magnetic and photo induced hyperthermia treatments</i>
15:10	<b>POSTER SESSION AND COFFEE</b> (main foyer)  <i>Free surface phenomena and FHD</i> <i>Heat and Mass Transfer</i> <i>Life science applications</i> <i>Magneto polymer composites</i> <i>Technological Applications</i>
16:30	
17:00	<b>OPTIONAL VISIT TO THE ALHAMBRA (EXTRA)</b> (Meeting point: Main Foyer at 16:30 h)

## WEDNESDAY JUNE 14 - MORNING SESSIONS

9:00	Chair: <u>James E. Martin</u>
	<b>PL-3. PLENARY LECTURE: <u>Orlin D. Velev</u></b> <i>Active, Ultraflexible and Reconfigurable Microstructures Powered by Magnetic Fields</i>
9:40	<b>MPC-OP-1. Oral - <u>Ramesh V. Upadhyay</u></b> <i>Influence of strain on the dynamic behaviour of magnetorheological elastomer</i>
9:55	<b>MPC-OP-2. Oral - <u>Andreas Menzel</u></b> <i>Induced changes in shape and transport properties of magnetic gels and elastomers</i>
10:10	<b>MPC-OP-3. Oral - <u>Mariusz Barczak</u></b> <i>Importance of the magnetic particles' functionalization in the design of ferrogels</i>
10:25	<b>MPC-OP-4. Oral - <u>Dmitry Borin</u></b> <i>Magnetic training of the soft magnetorheological elastomers</i>
10:40	<b>COFFEE BREAK</b> (Main foyer)
11:05	Chair: <u>Laura Rodríguez Arco</u>
	<b>KNL-4. KEYNOTE LECTURE: <u>Pietro Tierno</u></b> <i>Magnetic colloidal currents generated via exchange dynamics in a broken dimer state</i>
11:30	<b>MPC-OP-5. Oral - <u>Ainara Gómez</u></b> <i>Shape-morphing magnetoactive elastomers</i>
11:45	<b>MPC-OP-6. Oral - <u>Dirk Romeis</u></b> <i>Magneto-active composites: From microscopic structure to effective magnetization</i>
12:00	<b>MPC-OP-7. Oral - <u>Marius Reiche</u></b> <i>Vibration-driven mobile robots based on multipole magnetoactive elastomers</i>
12:15	<b>MPC-OP-8. Oral - <u>Gracia García-García</u></b> <i>Thermoresponsive core/shell nanoparticles for chemotherapy and phototherapy against cancer</i>
12:30	<b>MPC-OP-9. Oral - <u>Yuhiro Iwamoto</u></b> <i>Energy harvesting using permanent magnet elastomer</i>
12:45	<b>LUNCH</b> (Main foyer)



## WEDNESDAY JUNE 14 - AFTERNOON SESSIONS

14:15	Chair: <u>Ángel Delgado</u>
	<b>KNL-5. Keynote lecture: <u>Stefan Odenbach</u></b> <i>Can materials be smart? The fascination of magnetic hybrid materials</i>
14:40	Chair: <u>Stefan Odenbach</u>
	<b>MEDAL CEREMONY</b> (Aula Magna)
15:55	<b>COFFEE BREAK</b> (Main foyer)
16:20	Chair: <u>Ladislau Vékás</u>
	<b>KNL-6. Keynote lecture: <u>James E. Martin</u></b> <i>Applications of multiaxial magnetic fields</i>
16:45	<b>RS-OP-1. Oral - <u>Olga Volkova</u></b> <i>Discontinuous Shear Thickening (DST) transition with spherical iron particles coated by adsorbed brush polymer</i>
17:00	<b>RS-OP-2. Oral - <u>Guillermo Camacho</u></b> <i>Multiaxial toggled field self-assembly</i>
17:15	<b>RS-OP-3. Oral - <u>Antolii V. Nagorny</u></b> <i>Interaction of aggregates in ferrofluids according to small-angle scattering data</i>
17:30	Chair: <u>Dmitry Borin</u>
	<b>TA-OP-1. Oral - <u>Rico Huhnstock</u></b> <i>Reversible clustering and separation of magnetic particles in a microfluidic environment using engineered magnetic field landscapes</i>
17:45	<b>TA-OP-2. Oral - <u>Alejandro Rodríguez Barroso</u></b> <i>Magnetic tweezer optimization for multiplexed Microrheology measurements</i>
18:00	<b>TA-OP-3. Oral - <u>Mudra Jadav</u></b> <i>Magneto-dielectric properties of a bi-dispersed magnetic nanofluid</i>
18:30	<b>DISCOVERING GRANADA: A GUIDED TOUR OF THE CITY</b> (Meeting point: Main Foyer at 18:15 h)

## THURSDAY JUNE 15 - MORNING SESSIONS

9:00	Chair: <u>Pavel Kuzhir</u>
	<b>PL-4. Plenary lecture: <u>John Philip</u></b> <i>Recent Advances in the understanding of Thermal Properties of Magnetic Nanofluids</i>
9:40	<b>PP-OP-1. Oral - <u>Olivier Sandre</u></b> <i>Optimal size of iron oxide nanoflowers at 22 nm for magnetic hyperthermia</i>
9:55	<b>PP-OP-2. Oral - <u>Kinnari Parekh</u></b> <i>Monodispersed Mn<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> nanoclusters based magnetic fluid: Synthesis and characterization</i>
10:10	<b>PP-OP-3. Oral - <u>Peter Kopcansky</u></b> <i>Neutrons- useful tool for structural study of magnetic nanoparticles in magnetic fluids and their composites</i>
10:25	<b>PP-OP-4. Oral - <u>Veronika Lacková</u></b> <i>The collective ordering of the magnetic nanoparticles and their influence on the liquid crystal matrix</i>
10:40	<b>COFFEE BREAK</b> (Main foyer)
11:05	Chair: <u>Andrejs Cebers</u>
	<b>KNL-7. Keynote lecture: <u>Pavel Kuzhir</u></b> <i>Physical aspects of magnetic nanoparticle manipulation in environmental and biomedical applications</i>
11:30	<b>PP-OP-5. Oral - <u>Melvin Küster</u></b> <i>Varying nanoscale characteristics of a liquid magnet and its effect on the magnetic dynamics</i>
11:45	<b>PP-OP-6. Oral - <u>Juan Melchor</u></b> <i>Ultrasonic emission induced by magnetic fluid hyperthermia</i>
12:00	<b>PP-OP-7. Oral - <u>Malika Khelfallah</u></b> <i>Self-assembly and poisoning effect in binary ferrofluids: an experimental study</i>
12:15	<b>PP-OP-8. Oral - <u>Amal Nasser</u></b> <i>Structural and magnetic characterization of superparamagnetic iron oxide nanoparticles for magnetically controlled immune therapy</i>
12:30	<b>PP-OP-9. Oral - <u>Ana Carolina Moreno Maldonado</u></b> <i>Synthetic Magnetosomes: the development of a nanocarrier for a thermo-active drug respond</i>
12:45	<b>LUNCH</b> (Main foyer)

## THURSDAY JUNE 15 - AFTERNOON SESSIONS

14:15	Chair: <u>Peter Kopcansky</u>
	<b>KNL-8. Keynote lecture: <u>Alexey Snezhko</u></b> <i>Emergent dynamics and control of active magnetic fluids</i>
14:40	<b>PP-OP-10. Oral - <u>Nerea Sebastián</u></b> <i>Dynamics of domain formation in a ferromagnetic fluid</i>
14:55	<b>PP-OP-11. Oral - <u>Guntars Kitenbergs</u></b> <i>Tuning properties of phase-separated magnetic fluid with temperature</i>
15:10	<b>PP-OP-12. Oral - <u>Margaret Rosenberg</u></b> <i>Impact of Interparticle Interactions on the Dynamic Magnetic Response of Platelets</i>
15:25	<b>PP-OP-13. Oral - <u>Reinard Richter</u></b> <i>Long-Term Measurements of the Magnetization of Suspensions of Isolated Bacterial Magnetosomes</i>
15:40	<b>PP-OP-14. Oral - <u>Ben Erné</u></b> <i>Colloidal Stability of Ferrofluids at 10 T</i>
15:55	<p style="text-align: center;"><b>POSTER SESSION AND COFFEE</b> (main foyer)</p> <p style="text-align: center;"><i>Active systems</i> <i>Environmental Applications</i> <i>Physical Properties</i> <i>Rheology and Structures</i> <i>Synthesis</i> <i>Theory and Computer Simulations</i></p>
17:25	Chair: <u>Juan de Vicente</u>
	<b>KNL-9. Keynote lecture: <u>Masaaki Motozawa</u></b> <i>Investigation of Flow Characteristics of Magnetic Fluid under Magnetic Field by Ultrasonic Velocity Profiling Method</i>
17:50	<b>PP-OP-15. Oral - <u>Amelie Juhin</u></b> <i>Experimental investigation of magnetic and self-assembling properties of CoFe<sub>2</sub>O<sub>4</sub> nano-flowers</i>
18:05	<b>PP-OP-16. Oral - <u>Alexey Eremin</u></b> <i>Topologically-assisted self-assembly driven tilting in nematic liquid crystal hybrids with dendronised nanoparticles</i>
18:20	<b>PP-OP-17. Oral - <u>Raúl Rica</u></b> <i>Optical manipulation of magnetic microparticles</i>
20:00	<p style="text-align: center;"><b>GALA DINNER AND FLAMENCO SHOW</b> (Palacio de los Córdoba)</p>

## FRIDAY JUNE 16 - MORNING SESSIONS

9:30	Chair: <u>Antonio Figueiredo Neto</u>
	<p style="text-align: center;"><b>PHD AWARD CEREMONY</b> (Aula Magna)</p> <p>PhDTA-KNL-1. Keynote lecture: <u>Cristina Gila-Vilchez</u> <i>Magnetic hydrogels for regenerative medicine and technological applications</i></p> <p>PhDTA-OP-2. Oral: <u>Alvaro Romero-Calvo</u> <i>Low-Gravity Ferrohydrodynamics</i></p> <p>PhDTA-OP-3. Oral: <u>Patricija Hribar Boštjančič</u> <i>Mechanisms for colloidal stabilization of magnetic nanoplatelets</i></p>
10:45	<b>COFFEE BREAK</b> (Main foyer)
11:10	Chair: <u>Olivier Sandre</u>
	<p>KNL-10. Keynote lecture: <u>Andrejs Cebers</u> <i>Magnetic droplets and flexible filaments: models and numerical simulations</i></p>
11:35	<b>S-OP-1. Oral - <u>Marina Lázaro-Callejón</u></b> <i>Magneto-photothermal synergy applied to gold-coated magnetic nanorods</i>
11:50	<b>S-OP-2. Oral - <u>Darja Lisjak</u></b> <i>Stabilization of magnetic nanoplatelets in nonpolar solvents via dipolar interaction</i>
12:05	<b>S-OP-3. Oral - <u>Christoph Wesemann</u></b> <i>Water Transfer of Magnetic Nanoparticles with Different Morphologies using a Ligand Exchange Reaction with a Short-Chained Catechol Derivate</i>
12:20	<b>S-OP-4. Oral - <u>Jerome Depeyrot</u></b> <i>Magnetic fluorescent nanofluids obtained by a colloidal approach</i>
12:45	<b>LUNCH</b> (Main foyer)



## FRIDAY JUNE 16 - AFTERNOON SESSIONS

14:15	Chair: <u>Ramesh Upadhyay</u>
	<b>KNL-11. Keynote lecture: <u>Sofia Kantorovich</u></b> <i>Pros and Cons of Using Computer Simulations when Investigating Magnetic Soft Matter</i>
14:40	<b>AS-OP-1. Oral - <u>Charis Czichy</u></b> <i>Deformation behavior of magnetic alginate-methylcellulose hydrogels</i>
14:55	<b>AS-OP-2. Oral - <u>Andris Pāvils Stikuts</u></b> <i>Ferromagnetic filament shapes reveal their magnetoelastic properties</i>
15:10	<b>AS-OP-3. Oral - <u>Moritz A. Raphael</u></b> <i>Single particle tracking of heterofunctional active nanostructures in magnetic fields</i>
15:25	<b>AS-OP-4. Oral - <u>Joseph Tavecchi</u></b> <i>Flexible Magnetic Microcrosses with Programmable Actuation Modes</i>
15:40	<b>COFFEE BREAK</b> (Main foyer)
16:05	Chair: <u>Guillermo Iglesias</u>
	<b>TCS-OP-1. Oral - <u>Andrey Kuznetsov</u></b> <i>Magnetophoretic transport of nanoparticles in diluted and concentrated ferrofluids</i>
16:20	<b>TCS-OP-2. Oral - <u>Oksana Bilous</u></b> <i>Phase behaviour of ferrogranulates in an applied magnetic field</i>
16:35	<b>TCS-OP-3. Oral - <u>Pablo Palacios Alonso</u></b> <i>Unveiling the nanoparticle surface effects on AC magnetization: boosting magnetic transduction</i>
16:50	<b>TCS-OP-4. Oral - <u>Sebastian A. Altmeyer</u></b> <i>Ferrofluidic wavy Taylor vortices under alternating magnetic field</i>
17:05	<b>TCS-OP-5. Oral - <u>Alexey O. Ivanov</u></b> <i>Mathematical and Computer Modelling of the Effects of Interactions, Structure Formation, and Polydispersity on the Dynamic Magnetic Susceptibility and Magnetic Relaxation of Ferrofluids</i>
17:20	<b>TCS-OP-6. Oral - <u>Xiang Li</u></b> <i>A fractional step lattice Boltzmann method for complex interfacial behaviors of ferrofluids</i>
17:35	<b>CLOSING CEREMONY</b> (Aula Magna)

# INDEX OF ABSTRACTS

<b>1. Plenary Lectures</b>	<b>15</b>
<ul style="list-style-type: none"> <li>• PL-1–Ladislau Vékás–Pag. 16</li> <li>• PL-2–María del Puerto Morales–Pag. 17</li> <li>• PL-3–Orlin D. Velev–Pag. 18</li> <li>• PL-4–Jonh Philip–Pag. 19</li> </ul>	
<b>2. Keynote Lectures</b>	<b>20</b>
<ul style="list-style-type: none"> <li>• KNL-1–Antonio Martins Figueiredo Neto–Pag. 21</li> <li>• KNL-2–Christine Ménager–Pag. 22</li> <li>• KNL-3–Annette M. Schmidt–Pag. 23</li> <li>• KNL-4–Pietro Tierno–Pag. 24</li> <li>• KNL-5–Stefan Odenbach–Pag. 25</li> <li>• KNL-6–James E. Martin–Pag. 26</li> <li>• KNL-7–Pavel Kuzhir–Pag. 27</li> <li>• KNL-8–Alexey Snezhko–Pag. 28</li> <li>• KNL-9–Masaaki Motozawa–Pag. 29</li> <li>• KNL-10–Andrejs Cebers–Pag. 30</li> <li>• KNL-11–Sofia Kantorovich–Pag. 31</li> </ul>	
<b>3. PhD Thesis Award</b>	<b>32</b>
<ul style="list-style-type: none"> <li>• PhDTA-KNL-1–Cristina Gila-Vilchez–Pag. 33</li> <li>• PhDTA-OP-2–Álvaro Romero-Calvo–Pag. 34</li> <li>• PhDTA-OP-3–Patricija Hribar Boštjančič –Pag. 35</li> </ul>	
<b>4. Oral presentations by topic</b>	<b>36</b>
<ul style="list-style-type: none"> <li>• <b>Free Surface Phenomena and Ferrohydrodynamics</b> <span style="float: right;"><b>36</b></span> <ul style="list-style-type: none"> <li>• FSP&amp;FHD-OP-1–Guillaume Ricard–Pag. 37</li> <li>• FSP&amp;FHD-OP-2–Carlo Rigoni–Pag. 38</li> <li>• FSP&amp;FHD-OP-3–Jaakko Timonen–Pag. 39</li> </ul> </li> <li>• <b>Environmental Applications</b> <span style="float: right;"><b>40</b></span> <ul style="list-style-type: none"> <li>• EA-OP-1–Takuya Kuwahara–Pag. 41</li> <li>• EA-OP-2–Álvaro Gallo-Cordova–Pag. 42</li> <li>• EA-OP-3–Sawako Nakamae – Pag. 43</li> </ul> </li> <li>• <b>Heat and Mass Transfer</b> <span style="float: right;"><b>44</b></span> <ul style="list-style-type: none"> <li>• HMT-OP-1–Mikhail S. Krakov–Pag. 45</li> <li>• HMT-OP-2–Zhongwu Rong–Pag. 46</li> <li>• HMT-OP-3–Huei Chu Weng–Pag. 47</li> </ul> </li> <li>• <b>Life Science Applications</b> <span style="float: right;"><b>48</b></span> <ul style="list-style-type: none"> <li>• LSA-OP-1–Jean-Michel Siague–Pag. 49</li> <li>• LSA-OP-2–María Salvador–Pag. 50</li> <li>• LSA-OP-3–Tamara Pozo-Gualda–Pag. 51</li> <li>• LSA-OP-4–Oliver Reisen–Pag. 52</li> <li>• LSA-OP-5–Erzsébet Illés–Pag. 53</li> <li>• LSA-OP-6–Veronica Salgueiriño–Pag. 54</li> <li>• LSA-OP-7–Claudia Lozano-Pedraza–Pag. 55</li> <li>• LSA-OP-8–Carlos Frade-Gonzalez–Pag. 56</li> <li>• LSA-OP-9–Clara Marquina–Pag. 57</li> <li>• LSA-OP-10–Danny Villanueva-Alvaro–Pag. 58</li> <li>• LSA-OP-11–Guillermo Iglesias Salto–Pag. 59</li> </ul> </li> <li>• <b>Magneto-Polymer composites</b> <span style="float: right;"><b>60</b></span> <ul style="list-style-type: none"> <li>• MPC-OP-1–Ramesh V. Upadhyay–Pag. 61</li> <li>• MPC-OP-2–Andreas Menzel–Pag. 62</li> <li>• MPC-OP-3–Mariusz Barczak–Pag. 63</li> <li>• MPC-OP-4–Dmitry Borin–Pag. 64</li> </ul> </li> </ul>	

<ul style="list-style-type: none"> <li>• MPC-OP-5–Ainara Gómez–Pag. 65</li> <li>• MPC-OP-6–Dirk Romeis–Pag. 66</li> <li>• MPC-OP-7–Marius Reiche–Pag. 67</li> <li>• MPC-OP-8–Gracia García-García–Pag. 68</li> <li>• MPC-OP-9–Yuhiro Iwamoto–Pag. 69</li> </ul>	70
<ul style="list-style-type: none"> <li>• <b>Rheology and Structures</b> <ul style="list-style-type: none"> <li>• RS-OP-1–Olga Volkova–Pag. 71</li> <li>• RS-OP-2–Guillermo Camacho–Pag. 72</li> <li>• RS-OP-3–Antolii V. Nagorny–Pag. 73</li> </ul> </li> </ul>	74
<ul style="list-style-type: none"> <li>• <b>Technological Applications</b> <ul style="list-style-type: none"> <li>• TA-OP-1–Rico Huunstock–Pag. 75</li> <li>• TA-OP-2–Alejandro Rodriguez-Barroso–Pag. 76</li> <li>• TA-OP-3–Mudra Jadav–Pag. 77</li> </ul> </li> </ul>	78
<ul style="list-style-type: none"> <li>• <b>Physical Properties</b> <ul style="list-style-type: none"> <li>• PP-OP-1–Olivier Sandre–Pag. 79</li> <li>• PP-OP-2–Kinnari Parekh–Pag. 80</li> <li>• PP-OP-3–Peter Kopcansky–Pag. 81</li> <li>• PP-OP-4–Veronika Lacková–Pag. 82</li> <li>• PP-OP-5–Melvin Küster–Pag. 83</li> <li>• PP-OP-6–Juan Melchor–Pag. 84</li> <li>• PP-OP-7–Malika Khelfallah–Pag. 85</li> <li>• PP-OP-8–Amal Nasser–Pag. 86</li> <li>• PP-OP-9–Ana Carolina Moreno Maldonado –Pag. 87</li> <li>• PP-OP-10–Nerea Sebastián–Pag. 88</li> <li>• PP-OP-11–Guntars Kitenbergs–Pag. 89</li> <li>• PP-OP-12–Margaret Rosenberg–Pag. 90</li> <li>• PP-OP-13–Reinard Richter–Pag. 91</li> <li>• PP-OP-14–Ben Erné–Pag. 92</li> <li>• PP-OP-15–Amelie Juhin–Pag. 93</li> <li>• PP-OP-16–Alexey Eremin–Pag. 94</li> <li>• PP-OP-17–Raúl A. Rica–Pag. 95</li> </ul> </li> </ul>	96
<ul style="list-style-type: none"> <li>• <b>Synthesis</b> <ul style="list-style-type: none"> <li>• S-OP-1–Marina Lázaro–Pag. 97</li> <li>• S-OP-2–Darja Lisjak–Pag. 98</li> <li>• S-OP-3–Christoph Wesemann–Pag. 99</li> <li>• S-OP-4–Jerome Depeyrot–Pag. 100</li> </ul> </li> </ul>	101
<ul style="list-style-type: none"> <li>• <b>Active Systems</b> <ul style="list-style-type: none"> <li>• AS-OP-1–Charis Czichy–Pag. 102</li> <li>• AS-OP-2–Andris Pāvils Stikuts–Pag. 103</li> <li>• AS-OP-3–Moritz. A. Raphael –Pag. 104</li> <li>• AS-OP-4–Joseph Tavacoli–Pag. 105</li> </ul> </li> </ul>	106
<ul style="list-style-type: none"> <li>• <b>Theory and Computer Simulations</b> <ul style="list-style-type: none"> <li>• TCS-OP-1–Andrey Kuznetsov –Pag. 107</li> <li>• TCS -OP-2–Oksana Bilous–Pag. 108</li> <li>• TCS -OP-3–Pablo Palacios-Alonso–Pag. 109</li> <li>• TCS -OP-4–Sebastian A. Altmeyer–Pag. 110</li> <li>• TCS -OP-5– Alexey O. Ivanov–Pag. 111</li> <li>• TCS -OP-6– Xiang Li–Pag. 112</li> </ul> </li> </ul>	113
<ul style="list-style-type: none"> <li>5. <b>Poster Session 1 by topic</b> <ul style="list-style-type: none"> <li>• <b>Free Surface Phenomena and Ferrohydrodynamics</b> <ul style="list-style-type: none"> <li>• FSP&amp;FHD-PS1-1–Alexandra S. Vinogradova–Pag. 114</li> <li>• FSP&amp;FHD-PS1-2–Arlex Chaves-Guerrero–Pag. 115</li> <li>• FSP&amp;FHD-PS1-3–Yo Mizuta–Pag. 116</li> <li>• FSP&amp;FHD-PS1-4–Ali Lakkis–Pag. 117</li> </ul> </li> </ul> </li> </ul>	113

• <b>Heat and Mass Transfer</b>	<b>118</b>
• HMT-PS1-1–Sukhdev Mouraya –Pag. 119	
• HMT -PS1-2–Yasushi Ido–Pag. 120	
• <b>Life Science Applications</b>	<b>121</b>
• LSA-PS1-1–Losé Luis Arias–Pag. 122	
• LSA-PS1-2–Jean-Michel Siaugue–Pag. 123	
• LSA-PS1-3– Antonio M. Figueiredo Neto–Pag. 124	
• LSA-PS1-4–Kinnari Parekh –Pag. 125	
• LSA-PS1-5–Zhila Shaterabadi–Pag. 126	
• LSA-PS1-6–Zhila Shaterabadi–Pag. 127	
• LSA-PS1-7–Pablo A Rodriguez-Jimenez–Pag. 128	
• LSA-PS1-8–Pablo A Rodriguez-Jimenez –Pag. 129	
• LSA-PS1-9–Rafal Bielas–Pag. 130	
• LSA-PS1-10–Arkadiusz Józefczak–Pag. 131	
• LSA-PS1-11–Tamara Pozo-Gualda–Pag. 132	
• LSA-PS1-12–Matilde Fernández –Pag. 133	
• LSA-PS1-13–Claire Carvallo–Pag. 134	
• LSA-PS1-14–Zuzana Gazova–Pag. 135	
• LSA-PS1-15– Jordy Queiros Campos–Pag. 136	
• LSA-PS1-16–Viktória Varga–Pag. 137	
• LSA-PS1-17–Alberto Sola-Leyva–Pag. 138	
• LSA-PS1-18–Yahya Shubbak–Pag. 139	
• LSA-PS1-19–Erzsébet Illés–Pag. 140	
• LSA-PS1-20–Marine Sagastuy–Pag. 141	
• LSA-PS1-21–Guillermo R. Iglesias–Pag. 142	
• LSA-PS1-22–José Luis Arias–Pag. 143	
• LSA-PS1-23–Rosalía López-Méndez–Pag. 144	
• <b>Magneto-Polymer Composites</b>	<b>145</b>
• MPC-PS1-1– Darshan Kare Gowda–Pag. 146	
• MPC-PS1-2–Alberto León-Cecilla–Pag. 147	
• MPC-PS1-3–Dmitry Borin–Pag. 148	
• MPC-PS1-4–Naoki Okada–Pag. 149	
• MPC-PS1-5–Chiemi Oka–Pag. 150	
• MPC-PS1-6–Surojit Ranoo–Pag. 151	
• MPC-PS1-7–Maria Weißpflog–Pag. 152	
• MPC-PS1-8–Rudolf Weeber–Pag. 153	
• MPC-PS1-9–Atsuki Kobayashi–Pag. 154	
• MPC-PS1-10–Gracia García-García–Pag. 155	
• <b>Technological Applications</b>	<b>156</b>
• TA-PS1-1–Xiang Li–Pag. 157	
• TA-PS1-2–Fergus Hall–Pag. 158	
• TA-PS1-3–Miloš Šárpataky –Pag. 159	
• TA-PS1-4– Raul-Alexandru Szakal–Pag. 160	
• TA-PS1-5–Raul-Alexandru Szakal–Pag. 161	
• TA-PS1-6–Fereshteh Sohrabi–Pag. 162	
• TA-PS1-7–Masaaki Motozawa–Pag. 163	
<b>6. Poster Session 2 by topic</b>	<b>164</b>
• <b>Active Systems</b>	<b>164</b>
• AS-PS2-1–Bhagyashri Shinde–Pag. 165	
• AS-PS2-2–Jānis Cīmurs–Pag. 166	
• AS-PS2-3–Michal Kubík–Pag. 167	
• AS-PS2-4–Francisco J. Vazquez-Perez–Pag. 168	
• AS-PS2-5–Mojca Vilfan–Pag. 169	
• AS-PS2-6–Ekaterina Novak–Pag. 170	
• AS-PS2-7–Martins Brics–Pag. 171	



<ul style="list-style-type: none"> <li>• AS-PS2-8–José Luis Carrillo–Pag. 172</li> <li>• AS-PS2-9–Ana B. Bonhome-Espinosa–Pag. 173</li> <li>• AS-PS2-10–Alfredo Escribano-Huesca–Pag. 174</li> </ul>	
<ul style="list-style-type: none"> <li>• <b>Environmental Applications</b></li> <li> <ul style="list-style-type: none"> <li>• EA-PS2-1– Yusuke Asaka–Pag. 176</li> <li>• EA-PS2-2– Eduardo Ordoqui-Huesa–Pag. 177</li> <li>• EA-PS2-3–Sawako Nakamae–Pag. 178</li> </ul> </li> </ul>	175
<ul style="list-style-type: none"> <li>• <b>Physical Properties</b></li> <li> <ul style="list-style-type: none"> <li>• PP-PS2-1–Michal Rajňák–Pag. 180</li> <li>• PP-PS2-2–Elisa Sani–Pag. 181</li> <li>• PP-PS2-3–Matus Molcan–Pag. 182</li> <li>• PP-PS2-4–Vishakha Dave–Pag. 183</li> <li>• PP-PS2-5–Natália Tomašovičová–Pag. 184</li> <li>• PP-PS2-6–Melvin Küster–Pag. 185</li> <li>• PP-PS2-7–Joanes Berastegui–Pag. 186</li> <li>• PP-PS2-8–Hajnalka Nádasí–Pag. 187</li> <li>• PP-PS2-9–Hajnalka Nádasí–Pag. 188</li> <li>• PP-PS2-10–Ashok Kumar–Pag. 189</li> <li>• PP-PS2-11–Alena Jurikova–Pag. 190</li> <li>• PP-PS2-12–Martina Koneracka–Pag. 191</li> <li>• PP-PS2-13–Vlasta Zavisova–Pag. 192</li> <li>• PP-PS2-14–Nerea Sebastián–Pag. 193</li> <li>• PP-PS2-15–Natan Osterman–Pag. 194</li> <li>• PP-PS2-16–Maria Balasoíu–Pag. 195</li> <li>• PP-PS2-17–Reinhard Richter–Pag. 196</li> <li>• PP-PS2-18–Bárbara C. C. Pereira–Pag. 197</li> <li>• PP-PS2-19–Yasuhiro Sawahata–Pag. 198</li> </ul> </li> </ul>	179
<ul style="list-style-type: none"> <li>• <b>Rheology and Structures</b></li> <li> <ul style="list-style-type: none"> <li>• RS-PS2-1–Ramesh V. Upadhyay–Pag. 200</li> <li>• RS-PS2-2–Ainara Gómez–Pag. 201</li> <li>• RS-PS2-3–Bassam Jameel –Pag. 202</li> <li>• RS-PS2-4–Ladislau Vékás–Pag. 203</li> <li>• RS-PS2-5–Keito Fukuta–Pag. 204</li> <li>• RS-PS2-6–Barbara Stępień –Pag. 205</li> </ul> </li> </ul>	199
<ul style="list-style-type: none"> <li>• <b>Synthesis</b></li> <li> <ul style="list-style-type: none"> <li>• S-PS2-1–Mariia Savchenko–Pag. 207</li> <li>• S-PS2-2–Marina Lázaro –Pag. 208</li> <li>• S-PS2-3–Iryna Antal–Pag. 209</li> <li>• S-PS2-4–Martina Kubovcikova –Pag. 210</li> <li>• S-PS2-5–Iryna Khmara –Pag. 211</li> <li>• S-PS2-6–Mónica Jimenez-Carretero –Pag. 212</li> <li>• S-PS2-7–Carlos Frade-González –Pag. 213</li> <li>• S-PS2-8–Patrick Schütz –Pag. 214</li> <li>• S-PS2-9–Julia N. Majcherkiewicz –Pag. 215</li> <li>• S-PS2-10–Mariusz Barczak–Pag. 216</li> <li>• S-PS2-11– Oliwia Kapusta –Pag. 217</li> </ul> </li> </ul>	206
<ul style="list-style-type: none"> <li>• <b>Theory and Computer Simulations</b></li> <li> <ul style="list-style-type: none"> <li>• TCS-PS2-1–Andrejs Cebers–Pag. 219</li> <li>• TCS-PS2-2–Deniz Mostarac –Pag. 220</li> <li>• TCS-PS2-3–S. Helbig–Pag. 221</li> <li>• TCS-PS2-4–Ivan S. Novikau –Pag. 222</li> <li>• TCS-PS2-5–Jacob Maarek–Pag. 223</li> <li>• TCS-PS2-6–Margaret Rosenberg–Pag. 224</li> <li>• TCS-PS2-7–Xian Li–Pag. 225</li> </ul> </li> </ul>	218



# PLENARY LECTURES



# **Ferrofluids and ferrofluid driven manufacturing of new materials: advanced characterization and applications**

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In the first part of the talk a brief overview will be given on some early results and recent achievements of synthesis procedures of engineering and biocompatible ferrofluids, involving both single core and multi-core magnetic nanoparticle colloidal systems with organic non-polar, organic polar and aqueous dispersion media. The structural, colloidal stability, magnetic and flow behaviour of different types of ferrofluids are evidenced through the results of advanced characterization methods (TEM/HRTEM, SAXS, SANS, XPS, SLS, DLS, SALS, magnetometry and Mössbauer spectroscopy, rheo-and magneto-rheometry). The ferrofluid mediated manufacturing and tunable properties of new materials- magneto-responsive nanocomposite carriers, fibrous membranes and ferrofluid based magnetorheological fluids- will be presented along with their envisaged applications: magnetic detection/separation of biomaterials, heavy metal ion removal from residual waters, ferromagnetic stent targeting, semiactive seismic dampers. The last part of the talk is devoted to progress in developing high performance rotating seals and magnetorheological flow controller devices for energy related applications.

## Developing efficient processes towards safe magnetic nanoparticles for biomedicine, environmental remediation and catalysis

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The search for more efficient, scalable, reproducible and standardized synthesis methods able to control particle size and crystallinity is still a challenge in nanotechnology. The microwave-assisted process is an interesting alternative for the production of well-defined magnetic nanoparticles that are highly uniform and crystalline with diameters between 5 and 50 nm. Tuning of the size, chemical composition, and interstitial occupation of the ferrite structure offer a wide set of parameters to adjust the magnetic properties of the particles to the specific requirements for biomedical applications [1, 2]. The advantages of the microwave heating are mainly found in the improved product yields, shorter reaction times and reproducibility. Microwave irradiation provides a uniform rise in temperature over the whole reaction volume by coupling microwave energy to the molecules inside the reaction mixture. These particles found application in many different areas, from water remediation to NMR imaging and cell labelling for cancer therapy (Fig. 1) [3].

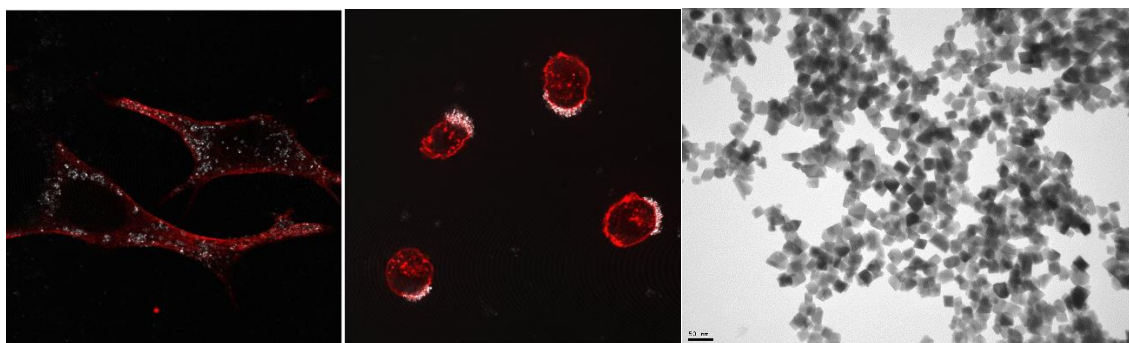


Fig. 1. Pan02 and Jurkat cells labelled with magnetic nanoparticles (bright spots) prepared by microwave heating in aqueous media.

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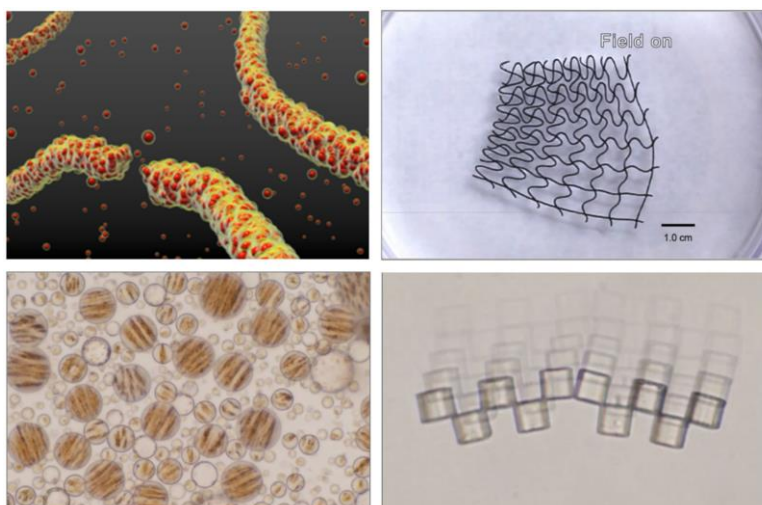
# Active, Ultraflexible and Reconfigurable Microstructures Powered by Magnetic Fields

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The use of magnetic fields is one of the most efficient means of assembling colloidal structures and manipulating their structure, interactions, and dynamics. More recently, it has become a convenient means of powering and controlling active colloidal structures and microbot prototypes. This talk will discuss a few classes of dynamically reconfigurable, active, and self-propelling magnetic colloidal structures. We will first discuss how the combination of magnetic assembly and nanocapillary liquid binding can be used to make ultraflexible and responsive filaments from lipid-coated nanoparticles suspended in water. Alternatively, the nanoparticle chains can be assembled and embedded inside silicone microbeads, resulting in a few types of soft micromagnets and microvoxels. These soft magnets can be incorporated into homocomposite thixotropic silicone pastes and can be directly shaped on a 3D printer to enable multiple classes of active magnetically reconfigurable structures. In the second part of the talk, we will discuss the principles of using magnetic assembly and actuation of dynamically reconfigurable active particle structures. We will show how assemblies of Janus polymer-metal microcubes can store energy through magnetic polarization of the metallic facets and release it on-demand by microscale reconfiguration. The reconfiguration pattern of folding and shape changes of the assemblies is encoded in the sequence of the cube orientation. Such structures can be directionally moved, steered, and maneuvered by external magnetic fields, acting as prototypes of microbots, micromixers and other active microstructures. These reconfigurable clusters can also be designed to be self-motile in media with non-Newtonian rheology. Such active assemblies can serve as microtools for interfacial studies in liquid crystal and biological systems.



# **Recent Advances in the understanding of Thermal Properties of Magnetic Nanofluids**

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New materials with unique properties are required to meet the new challenges of modern technologies. Among various new materials emerged over the years, magnetic nanofluids or ferrofluids have been at the forefront of research because of their interesting physiochemical properties and technological applications. Technological advancement and miniaturization of electronic gadgets fueled intense research on nanofluids as potential candidates for cooling applications as a substitute to conventional heat transfer fluids. Among nanofluids, magnetic nanofluid have attracted a lot of attention owing to their magnetic field tunable thermal conductivity in the presence of the magnetic field. The field-induced aggregates act as low resistance pathways thereby improving thermal transport substantially. Recent studies show that ferrofluids with smaller size and narrow size distribution display significant enhancement in thermal conductivity in the presence of a magnetic field with negligible viscosity enhancement, which is ideal for effective thermal management of electronic devices, especially in miniature electronic devices. On the contrary, highly polydisperse ferrofluids containing large aggregates, show modest enhancement in thermal conductivity in the presence of a magnetic field and a huge enhancement in viscosity. The most recent studies show that magnetic field ramp rate has a profound effect on aggregation kinetics and thermal and rheological properties. The viscosity enhancement under an external stimulus impedes their practical use in electronics cooling, which warrants the need to attain a high thermal conductivity to viscosity ratio, under a modest magnetic field. In my talk, I will talk about the recent advances in the field of thermal properties of magnetic fluids.



# KEYNOTE LECTURES



# Nonlinear optical properties of magnetic fluids: from single particle to the collective behavior

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Magnetic colloids are an interesting class of materials to investigate nonlinear optical properties of nanoparticles. The external magnetic field can be employed to orient single particles and impose the formation of different types of aggregates, from linear chains to bundles. In these conditions, the electric field (e.g., from light) can be oriented parallelly and perpendicularly to the external magnetic field, to investigate anisotropies on the nonlinear response of the particles alone or in clusters. One of these parameters is the first-order hyperpolarizability ( $\beta_H$ ), which is present in the energy ( $U$ ) of a dipole ( $\vec{P}$ ) in the presence of an external electric field ( $\vec{E}$ ):  $U = U_0 - P_i E_i - \alpha_{ij} E_i E_j - \beta_{Hijk} E_i E_j E_k$ . Assuming, now, an ensemble of dipoles in the magnetic colloid, the third-order electric susceptibility ( $\chi^{(3)}$ ) is present in the expression of the electric polarization:  $P = \chi^{(1)} E + 2\chi^{(2)} EE + 3\chi^{(3)} |E|^2$ . The first-order hyperpolarizability  $\beta$  of magnetite nanoparticles in colloidal dispersion was measured in the presence and absence of an external magnetic field of magnitude  $H = 800$  G. For that, the (linear) attenuation spectrum was measured, and the nonlinear properties were obtained through the hyper-Rayleigh scattering technique. The attenuation spectrum is the same, regardless of the external magnetic field, indicating that large aggregates of nanoparticles were not formed on our system. The first-order hyperpolarizability, on the other hand, increased when the incident laser-beam polarization was parallel to the magnetic field, and decreased when the directions were orthogonal. This is due to the alignment of the crystallographic planes of the material when nanoparticles rotate, in order to align their individual magnetic momentum with respect to the external field. For the parallel case,  $\beta_{H\parallel} = 9.8(2) \times 10^{-28} \text{ cm}^5/\text{esu}$ , while for the perpendicular configuration,  $\beta_{H\perp} = 8.1(1) \times 10^{-28} \text{ cm}^5/\text{esu}$ . Defining the x axis of the particle reference frame parallel to the  $\langle 111 \rangle$  crystallographic direction, which corresponds to the direction of easy magnetization,  $\beta_{H\parallel} = \beta_{Hxxx}$ , and  $\beta_{H\perp}$  corresponds to an average from  $\beta_{Hyyy}$ , and  $\beta_{Hzzz}$ . The Real and Imaginary parts of  $\chi^{(3)}$  of magnetite nanoparticles were also measured by using, now, the Z-Scan technique. The nonlinear index of refraction and absorption are of the order of  $-14 \times 10^{-14} \text{ cm}^2/\text{W}$  and  $1.5 \text{ cm}/\text{GW}$ , respectively. An anisotropy was also observed in the  $\chi^{(3)}$  measurements, as observed in the measurements of  $\beta_H$ .

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# How magnetic nanoparticles can reach the cytosol?

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Magnetic nanoparticles (MNPs), as any other type of nanoparticles, are internalized by cells through endocytosis, and thus are trapped in intracellular vesicles called endosomes<sup>[1]</sup>. But for a number of bio-applications, such as cellular engineering or magnetic hyperthermia treatments, it can be of great interest to have particles able to reach the cell cytoplasm. This would allow to have less dipolar interactions between the MNPs, and hence increase their intracellular heating properties<sup>[2]</sup>. It would also enable the possible diffusion of the MNPs in the cytosol and the targeting of specific intracellular proteins of organelles, which would open the door to intracellular engineering with MNPs.

We will give some recent examples of magnetic manipulation after injection of functionalized MNPs inside cells<sup>[3,4]</sup>. However, injection of MNPs limits their future applications. Other strategies must be envisioned in order to avoid the endosomal entrapment. Among them, one can cite the use of anisotropic MNPs, the development of liposomes able to fuse with the plasma membrane or the design of MNPs capable of endosomal escape, strategy that we have recently developed. The objective was to improve the access of MNPs to the cytosol by functionalizing them with cationic peptides. It has been demonstrated that sequences rich in histidine residues promote endosomal escape by proton sponge effect. Core-shell particles  $\gamma\text{-Fe}_2\text{O}_3@ \text{SiO}_2$  were functionalized by cationic peptides using click chemistry. After careful characterization of the functionalized MNPs, we showed, by means of confocal microscopy and transmission electron microscopy, that the poly-histidine peptide promoted cytosol access to the MNPs probably through the proton sponge effect<sup>[5]</sup>.

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# Universality in Ferronematic Liquids: Polymer-mediated Stabilization of Magnetic Nanodopants of Different Size and Shape in Liquid Crystal Phases

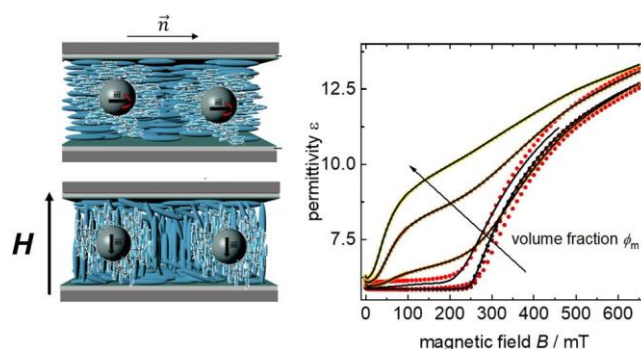
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Many liquid-crystalline (LC) systems can readily be manipulated by the use of external fields, inherent from the overall soft performance, and the anisotropic nature of the mesogens. The phenomenon is well exploited for electric field effects (Fréedericksz transition), while it requires enormous magnetic fields to switch common molecular mesogens directly, using a tiny anisotropy in susceptibility of the phases.

In 1970, Brochard and de Gennes [1] postulated the concept of doping molecular LC matrices with anisotropic nanoparticles in order to enhance their response to external magnetic fields, leading to a new class of ferronematic or ferrocholesteric phases. Up to date, experimental evidence for a significant magnetic Fréedericksz transition in moderate fields is limited to a few examples. A critical parameter is the coupling energy between the particle surface and the liquid crystalline matrix. A promising approach recently developed in our lab is the surface modification of spindle-like particles as the most important step in creating an effective coupling condition. For this purpose, a polymeric backbone is employed as connection agent, realizing side-chain liquid crystal polymer ligands on the particle surface. A combination of analytical techniques including light scattering, magnetometry, polarization microscopy and calorimetry is used to thoroughly investigate the resulting particle / matrix systems and to quantify the evolving coupling effect and the field response of the ferronematic phase. Based on theoretical considerations, a generalization of the principle and a model for the molecular coupling mechanism is presented.



**Fig. 1.** Concept and experimental verification of magnetically doped ferronematic phases based on molecular mesogens and polymer-decorated MNPs.

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# Magnetic colloidal currents generated via exchange dynamics in a broken dimer state

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In this talk, I will describe a general strategy to assemble and transport polarizable magnetic microspheres in fluid media through a combination of confinement [1] and magnetic dipolar interactions [2]. We use a homogeneous magnetic modulation to assemble dispersed particles into rotating dimeric state and frustrated binary lattices and generate collective edge currents that arise from a novel, field-synchronized particle exchange process [3]. The observed, net bidirectional current is composed of colloidal particles which periodically meet assembling into rotating dimers, and exchange their positions in a characteristic, "ceilidh"-like dance. We develop a theoretical model that explains the physics of the observed phenomena as dimer rupture and the onset of current, showing agreement with Brownian dynamic simulations [4]. Further, we recently explore the transport of defects as non-magnetic inclusions in ferrofluids media and the anomalous dynamics of the broken/recombining dimers during the exchange process. Overall, we demonstrate an effective technique to drive microscale matter by using the interplay of steric confinement and dipolar forces, not based on any gradient of the applied field.

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# Can materials be smart?

## The fascination of magnetic hybrid materials

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The term "Smart Materials" has been used for many years both in scientific literature and in the press in general. This raises the question of what is meant by "smart materials"? If one looks at the literature here, it is generally assumed that these are materials whose properties can be altered by external stimuli. The number of possible stimuli is unbelievably large.

If one looks at materials whose influence can be technically used, magnetic hybrid materials represent a prototype of the "smart materials" class. These materials, which consist of magnetic nano- or microparticles in a non-magnetic matrix, can be controlled by the effect of magnetic fields.

If a simple Newtonian liquid is chosen as the matrix material, ferrofluids or magnetorheological fluids are obtained depending on whether magnetic nanoparticles or microparticles are used. The change in particle size alone leads to significant changes in material behavior in the magnetic field. While ferrofluids not only allow a change of their properties in the field but also an active magnetic flow control, magnetorheological fluids can be used to set a magnetically induced yield stress, e.g. for technically relevant force transmissions.

The possibility of influencing the material properties becomes even more extensive if more complex materials for the non-magnetic matrix are used instead of a simple Newtonian fluid. Liquid crystals, polymer solutions or blood can significantly expand the spectrum of liquid magnetic hybrid materials - even with a clearly application-relevant focus.

If elastomers or gels are used instead of fluid matrix materials, a new class of materials is generated that has been researched for about 15 years and is usually referred to as magnetic elastomers. In these materials, both the modulus of elasticity can be influenced by magnetic fields and actuator deformations of the material can be induced. With these materials, too, the possibility of varying the magnetic as well as the non-magnetic component offers the opportunity to produce tailor-made materials for specific applications.

However, the targeted adjustment of material properties requires a detailed, cross-scale understanding of material behavior. At this point, variations in material behavior must be combined with microstructural changes, for which e.g. X-ray microtomography is an excellent tool.

In the context of the talk especially the use of X-ray microtomography for microstructural investigations and the link of such data to macroscopic properties will be discussed.

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# Applications of multiaxial magnetic fields

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Multiaxial magnetic fields, consisting of mutually orthogonal field components, are a powerful and flexible means of controlling magnetic fluids. One of the most interesting and useful effects is the generation of vigorous fluid vorticity by applying a triaxial field consisting of frequencies whose ratios can be expressed by small integers, e.g. 1:2:3. In contrast to magnetohydrodynamics, whose mechanism is the Lorentz force on charges moving through a magnetic field, this fluid motion is due to symmetry aspects of the union of the magnetic field trajectory and its converse. [1, 2] In the simplest case, the induced vorticity is stationary, the vorticity vector being fixed in magnitude and direction. But phase modulation of one or two of the field components can create fluid vorticity that oscillates, which is a 1-d trajectory of the vorticity vector. By applying a dc bias to one of three carefully chosen field components it is possible to create a "field symmetry transition" that results in a limitless variety of 3-d vorticity vector orbits when one or two of the field components are phase modulated. [3] In addition to the utility of these orbits to fluid mixing and heat and mass transfer, they can be to create highly-ordered particle composites when the fluid is a polymerizing resin. Examples of these effects will be shown, and a particle-based model of fluid vorticity will be described. [4]

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# **Physical aspects of magnetic nanoparticle manipulation in environmental and biomedical applications**

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Microfluidic manipulation of magnetic nanoparticles (MNP) is a smart tool for various environmental and biomedical applications. In most of these applications, MNP carry on their surface adsorbed molecules (micropollutants or biomolecules) that need to be either delivered to a specific site (controlled drug delivery, gene transfection) or extracted from the solvent (immunoassays, protein purification, water purification). Unfortunately, these techniques have a strong limitation related to the low efficiency of magnetic manipulation of MNP due to their Brownian motion and the low separation efficiency from the suspending fluid (magnetic separation) under flow in microfluidic circuits. However, molecules adsorbed on the surface of MNP can reduce the repulsive colloidal interactions between them and cause their weak agglomeration. Such agglomeration in the absence of an applied magnetic field leads to an increase in the effective size of the nanoparticles (or rather the primary aggregates). Once the magnetic field is applied, the magnetic force exerted on the primary aggregates will be strongly amplified compared to the case of individual non-aggregated MNP. In this case, the adsorbed molecules not only fulfil their function in the intended applications, but also provide a significant improvement in the remote control over the MNP by the magnetic fields, thus broadening the scope of MNP applications.

In this communication, we report the effects of the properties and quantities of the adsorbed molecules on the efficiency of the microfluidic magnetic separation of iron oxide nanoparticles (IONP). Our initial postulate on the adsorption-enhanced magnetic separation of MNP is checked on three different physicochemical systems covering different application: (i) methylene blue cationic dye adsorbed on citrate coated IONP for water purification; (ii) curcumin bound to the beta-cyclodextrin modified IONP for magnetic drug delivery; (iii) antigens bound to IONP decorated with antibodies for model immunoassays. We find striking similarities of the magnetic-field induced behaviors of these different systems, with the dipolar coupling parameter, the supersaturation and the Mason number being the main governing parameters. We also mention the possibility of using this concept for enhancement of the convective drug transport through the blocked blood vessels and for the formation of dense aggregates hampering ionic transport during electrolytic processes.

# Emergent dynamics and control of active magnetic fluids

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Active magnetic matter, demonstrates complex spatiotemporal self-organization and the emergence of collective behavior. We demonstrate that ferromagnetic microparticles suspended at an air-water interface and energized by an external rotating magnetic field spontaneously form dynamic ensembles of synchronized self-assembled spinners in a certain range of the excitation field parameters. Collective interactions of the multiple spinners forming a magnetic spinner liquid promote the formation of dynamic lattices. On the basis of experiments and simulations, we reveal structural transitions from liquid to nearly crystalline states in this novel active spinner material and demonstrate that dynamic spinner lattices are reconfigurable and capable of self-healing behavior [1]. A coherent rotational motion, the vortex phase, is of great interest because of its ability to orchestrate well-organized motion of self-propelled particles over large distances. However, its generation without geometrical confinement has been a challenge. We demonstrate by experiments and computational modeling that concentrated magnetic roller liquids [2, 3] energized by an external uniaxial alternating magnetic field self-organize into a state with multiple long-lived vortices in unconfined environment [3, 4]. We show that spontaneous dynamic local magnetic roller densifications trigger the formation of multiple vortices in an unconfined environment. We show that the neighboring vortices more likely occur with the opposite sense of rotation. The studies provide insights into the mechanism for the emergence of coherent collective motion on the macroscale from the coupling between microscale rotation and translation of individual magnetic active elements. Our findings provide insights into the behavior of active magnetic liquids with reconfigurable structural order and tunable functionalities.

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# Investigation of Flow Characteristics of Magnetic Fluid under Magnetic Field by Ultrasonic Velocity Profiling Method

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Velocity information is quite important one for analysis of characteristic flow phenomena. There are many techniques for measuring flow velocity such as optical methods (e.g. Laser Doppler Velocimetry (LDV) and Particle Image Velocimetry (PIV) etc.), electrical methods (Hot-wire etc.) and so on. However, because a magnetic fluid is a black opaque fluid, it is difficult to apply some conventional methods. Ultrasonic Velocity Profiling (UVP) Method, which is developed by Takeda [1] more than 30 years ago, is a technique for measuring a velocity profile by using ultrasound. The basic principle of UVP method is a way of consisting a velocity profile along the ultrasonic beam from the ultrasonic Doppler shift frequency. As this method used ultrasound to measure the flow velocity, there are some advantages comparing with conventional measurement techniques as follows;

- ✓ Line measurement
- ✓ To apply opaque fluid
- ✓ To obtain the velocity information in almost real-time.

The details of UVP technique can be found in Ref. [2].

After the development of UVP method, many researchers applied the UVP method to analyze the flow velocity of opaque fluid such as liquid metal, chemical substances, organic fluids and food materials etc. In the case of magnetic fluid, Sawada et al. [3] and Kikura et al. [4] applied the UVP method to actual velocity profile measurement of magnetic fluid sloshing and Taylor vortex flow of magnetic fluid, respectively. In my previous work, the UVP method is applied to oscillating pipe flow of magnetic fluid [5], rectangular duct flow of magnetic fluid including heat transfer phenomenon [6], and analysis of turbulent structure of magnetic fluid [7]. On the other hand, it is necessary to have an accurate ultrasonic velocity in a magnetic fluid when applying UVP method to magnetic fluid flow. However, the ultrasonic propagation velocity of magnetic fluid changes by applying external magnetic field [8]. Therefore, ultrasonic propagation properties of magnetic fluid are also important for application of the UVP method to magnetic fluid flow. In my presentation, principle of the UVP method, ultrasonic propagation properties in magnetic fluid, some actual measurements of magnetic fluid flow by the UVP method will be introduced.

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# **Magnetic droplets and flexible filaments: models and numerical simulation**

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An important and difficult problem of magnetic liquids is their figures of equilibrium as determined by the balance of capillary, magnetic ponderomotive forces and gravity. As opposed to the case of self-gravitating rotating masses, in the case of magnetic liquids the exact analytical solutions are not known and the numerical methods become the most efficient tool for solving the problem. As the first example we can mention the simulation of labyrinthine structures by applying the boundary integral equation technique. The labyrinthine patterns observed motivated the consideration of the case of the interface between miscible magnetic and nonmagnetic fluids realized in Hele-Shaw cells. The resulting motion was termed magnetic microconvection and is simulated by pseudospectral methods for the coupled set of equations for the concentration, velocity and magnetic fields. One of the first problems considered from the point of view of equilibrium shapes of magnetic fluid is the shape of droplet in an applied field. Solving it gives access to the physical properties of the magnetic liquid – its permeability, surface tension and others. For the simulation a boundary integral equation technique for the coupled velocity and magnetic fields was developed. A very rich class of phenomena takes place in the case when magnetic droplets are under the action of the rotating field. Let us give few examples. Magnetic droplet under the action of the high frequency rotating field has a series of bifurcations with increasing field strength: oblate, prolate (triaxial), back to oblate and finally to the star-fish configuration. In the limit of small deformations the shape of the droplet may be described by the symmetric second rank tensor (anisotropy tensor), the eigenvalues of which give the semi-axes of the ellipsoidal droplet and their orientation. The phenomenological relaxation equation for the anisotropy tensor may be formulated which contains the capillary relaxation time, magnetic Bond number and the frequency of the rotating field. The model gives the parameters of the droplet in the steady case (elongation, flatness, orientation) in dependence on the frequency of the rotating field which are in a good agreement with the numerical solution. Among the results obtained we can mention the transient regime when the droplet, similarly to the damped oscillator, makes several revolutions before reaching the stable focus corresponding to the steady case and the regime of pseudo-rotation without applied torque due to its shape deformation. Interesting properties are also exhibited by an ensemble of rotating droplets which, starting from disorder, forms a hexagonal structure that rotates with an angular velocity less than that of the single droplets. Rows of disclinations separating grains with different orientations of axes are observed. Numerical simulation of rotating crystals is carried out by solving the Stokesian hydrodynamics of a 2D ensemble of rotlets. If the droplets interact only hydrodynamically they remain in a disordered state. The introduction of repulsive interactions causes the ordering of the droplets in a hexagonal structure. It is curious that two ensembles initially at some distance from each other rotate as a pair of rotlets around their centre of mass and with the increase of time merge, forming a disordered state. The merging process ends with a single rotating crystal. In the second part flexible magnetic rods are considered. In the general case, the coupled set of the equations of elasticity, hydrodynamics and electromagnetism should be solved. Different approximations used in this case will be described.

# Pros and Cons of Using Computer Simulations when Investigating Magnetic Soft Matter

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The idea of creating magnetically controllable colloids whose rheological properties can be finely tuned on the nano- or micro-scale has caused a lot of experimental and theoretical effort [1]. The latter resulted in systems whose building blocks are ranging between single magnetic nanoparticles to complexes of such nanoparticles bound together by various mechanisms.

It turned out that computer simulations can be successfully used to predict equilibrium properties of magnetic fluids, magnetic polymer-like structures, magnetic gels and elastomers, magnetic anisotropic and anisometric particles [2-7]. First results are also obtained for dynamic properties of mono disperse suspensions of magnetic nanoparticles [8]. What is not yet clear, albeit being of primary interest, it is how the dynamics of the systems of anisotropic and an isometric particles or of magnetic particles embedded in one or another way into polymer matrices is affected by their intrinsic features.

Here I will discuss potential and limitations of coarse-grained molecular dynamics simulations combined with three different approaches based on egg-model [9], hot Stoner-Wolfarth paradigm [10] and extended dipoles [11] to allow for particle magnetic nature, as well as with Lattice-Boltzmann method to take into account hydrodynamics. I will discuss, anisotropic and anisometric magnetic particles, magnetic polymer-like structures and magnetic elastomers in my contribution.

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PhD THESIS  
AWARD



# Magnetic hydrogels for regenerative medicine and technological applications

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Hydrogels are defined as three-dimensional (3D) networks of flexible polymer chains dispersed in an aqueous medium. Due to their flexibility, softness, high water content and the versatility of their mechanical properties, hydrogels are used for several applications in technology and biomedicine. Due to their composition, magnetic hydrogels, which consist of dispersions of magnetic micro or nanoparticles embedded within a hydrogel, combine in a single material the paramagnetic or ferromagnetic behavior provided by the particles with the flexibility provided by the matrix. The properties of magnetic hydrogels depend on several factors, including the type of gelling agent and magnetic particles, their concentration, and the size and distribution of the magnetic particles within the hydrogels. Furthermore, magnetic particles are solid substrates that can be coated and functionalized for different purposes. The chemical nature of the coating layer can modulate the interactions between the particles and the polymer filaments that form the hydrogels, which has a direct impact on the final properties of the resulting hydrogels.

Thus, new magnetic hydrogels able to modify, to a great extent, or reversibly modulating their mechanical properties, are needed. Furthermore, the understanding of how to precisely control cellular organization and vascularization in complex tissue constructs is still in a preliminary state. Finally, injectable hydrogels are crucial for biomedical applications, since injectability is the main requirement to implement minimally invasive surgical methods.

The starting hypothesis of this work is that it is possible to prepare injectable magnetic hydrogels, based on short-chain peptides and/or polymers, with a microstructure and mechanical properties suitable for use both in technological applications and in the creation of extracellular matrices of soft artificial tissues. Therefore, this doctoral thesis aims to solve two of the main disadvantages of current injectable hydrogels: (i) the lack of an adequate microstructure; (ii) poor control over its mechanical properties. These general objectives are addressed simultaneously from the physical and chemical points of view, in order to create new hydrogels with better properties. We synthesized a diverse spectrum of supramolecular and polymeric magnetic hydrogels with adequate internal order due to the nature of the fibers, their interaction with the magnetic particles, and their arrangement.

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# Low-Gravity Ferrohydrodynamics

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The space community is undergoing an accelerated transformation boosted by the commercialization of the sub-orbital domain, the ambition to make humans a multi-planetary species, and the need for more sustainable space operations. Traditional technical solutions are being revealed as insufficiently robust, efficient, or reliable in an increasingly demanding technical context. Of particular interest are fluid management devices due to their central role in life support, material processing, in-situ resource utilization, or propellant positioning.

Low-gravity fluid systems are largely based on surface tension and rotary devices that fail to meet the performance and/or safety requirements featured in upcoming missions. A potential solution lies in the development of a new generation of touchless electromagnetic actuation mechanisms. Magnetic polarization provides an inhomogeneous mid-range force that enables the control of multiphase flows in space without moving parts. Applications include magnetic positive positioning, magnetic liquid sloshing, propellant management, mass transfer, and, in general, phase separation.

The term *low-gravity ferrohydrodynamics (LG-FHD)* is introduced as the extension of the capillary multiphase flow theory to magnetically polarized liquids, such as ferrofluids. The LG-FHD domain has distinctive characteristics that complicate analytical and numerical approximations. For very susceptible liquids (e.g. ferrofluids), a strong coupling arises between the Navier-Stokes and Maxwell governing equations which must be solved using an appropriate scheme. In addition, the solution depends on a spatially inhomogeneous magnetic force potential. This is a key novelty in the study of low-gravity fluid mechanics, where most potential fields are one-dimensional. As with capillary flows, however, the small gravity-to-surface tension ratio (or Bond number) drives the behavior of the interface.

In this presentation, the distinctive characteristics and applications of LG-FHD are discussed with a focus on the equilibrium, stability, and modal response of axisymmetric liquid-gas interfaces. Partially coupled analytical approximations are derived following the track of the classical literature in low-gravity fluid mechanics [1]. Their validity is assessed by employing microgravity experiments with water-based ferrofluids carried out at ZARM's drop tower, showing that only a fully coupled approximation to the capillary ferrohydrodynamic problem can accurately predict the modal response of the interface. This motivates the recent development of the very first fully coupled interface-tracking multiphase ferrohydrodynamic model [2], which is described and compared with the analytical formulations. The particular case of a low-susceptibility liquid is presented due to its relevance for bubble and droplet dynamics, which are assessed with dedicated formulations and microgravity experiments [3].

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# Mechanisms for colloidal stabilization of magnetic nanoplatelets

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Colloidal suspensions of ferrimagnetic barium hexaferrite (BHF) nanoplatelets (NPLs) present a complicated system due to the presence of magnetic dipole-dipole interactions that lead to aggregation. Colloidal stability is crucial for the preparation of ferromagnetic liquids that exhibit spontaneous magnetization in the absence of an external magnetic field due to spontaneous orientational ordering of the NPLs in an isotropic solvent [1] or a nematic liquid crystal [2]. First, we investigated electrostatic interactions between BHF NPLs modified with dodecylbenzenesulfonic acid in four alcohols [3]. We measured zeta potential, determined the concentration of the free surfactant, and calculated the Debye length, which was the basis for the calculation of electrostatic and average interaction energy between the NPLs in alcohols. Based on the calculations, we chose 1-butanol to be the best solvent to prepare highly stable ferromagnetic ferrofluids and determine the isotropic-nematic phase transition concentration in dependence of the equivalent diameter distribution, magnetization, and surfactant concentration [4]. The fundamental understanding of the interplatelet interactions in isotropic alcohol suspensions gained in the first part enabled the preparation of stable colloidal suspensions (ferromagnetic liquids) in non-alcoholic solvent and in a nematic host as well.

## Acknowledgments

This work was funded by the Slovenian Research Agency (research core funding No. P1-0192, P2-0089, P1-0201 and research projects No. PR-08415, J1-2459, J7-8267, N2-0118).

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# ORAL PRESENTATIONS

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Free Surface Phenomena & Ferrohydrodynamics



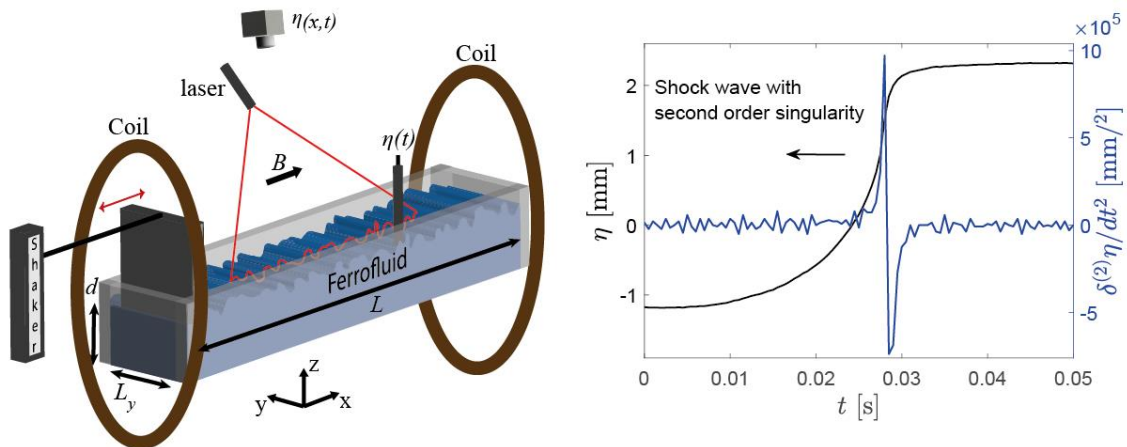
# Transition from wave turbulence to acousticlike shock wave regime

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Wave turbulence is a statistical state in which numerous random weakly nonlinear waves interact with each other. It leads to an energy cascade from large scales down to small scales driven by resonant interactions between waves. This state is first evidenced experimentally in a one-dimensional canal for dispersive gravity-capillary waves on the surface of mercury [1]. Then by using a ferrofluid and a high external magnetic field, we observe experimentally a transition from dispersive wave turbulence to a nondispersive regime involving coherent structures which are found to be shock waves [2]. Such a structure is characterized by a significant steepening with a discontinuity, and corresponds to a singularity in its second-order derivative. Because of the discontinuities, these shock waves are rich in the frequency domain, and carry energy over the canal. They thus become the main mechanism building the wave energy spectrum.



## Acknowledgments

This work was supported by the French National Research Agency (ANR DYSTURB Project No. ANR-17-CE30-004 and ANR SOGOOD Project No. ANR-21-CE30-0061-04), and the Simons Foundation MPS No. 651463–Wave Turbulence (USA).

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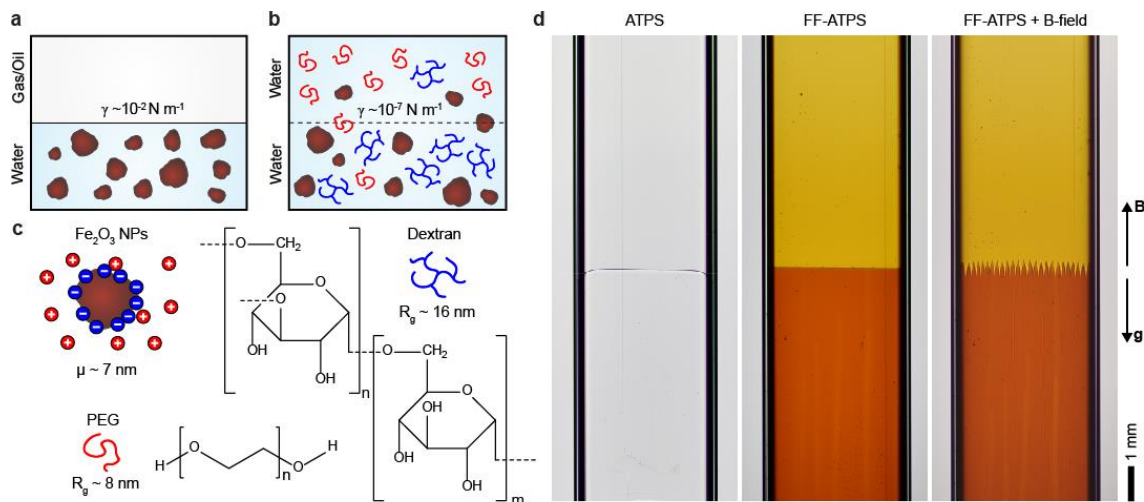
# Ferrofluidic aqueous two-phase system with ultralow interfacial tension and micro-pattern formation

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Ferrofluids are magnetic liquids known for the patterns they form in external magnetic fields. Typically, the patterns form at the interface between a ferrofluid and another immiscible non-magnetic fluid with a large interfacial tension  $\gamma \sim 10^{-2} \text{ Nm}^{-1}$ , leading to large pattern periodicities. In this presentation related to a recently published publication [1] we show that it is possible to reduce the interfacial tension several orders of magnitude down to ca.  $\gamma \sim 10^{-6} \text{ Nm}^{-1}$  by using two immiscible water-based phases based on spontaneous phase separation of dextran (Dex-T500) and polyethylene glycol (PEG 35000) and the asymmetric partitioning of superparamagnetic maghemite nanoparticles into the dextran-rich phase. The system exhibits classic Rosensweig instability in uniform magnetic field with periodicity  $\sim 200 \mu\text{m}$ , significantly lower than in traditional systems ( $\sim 10 \text{ mm}$ ). This system paves the way towards the science of pattern formation at the limit of vanishing interfacial tension and ferrofluid applications driven by small magnetic fields.



**Figure.** Scheme and experimental realization of a ferrofluidic aqueous two-phase system (FF-ATPS). **a**, A scheme of a regular water-based ferrofluidic system. **b**, A scheme of the FF-ATPS. **c**, Components of the FF-ATPS system and structural formulas of PEG and dextran. **d**, Photographs of a standard PEG-dextran ATPS (left), a maghemite-PEG-dextran FF-ATPS (center) and the same maghemite-PEG-dextran FF-ATPS in a vertical magnetic field of 20.0 mT exhibiting a quasi-1D magnetic instability at the interface (right).

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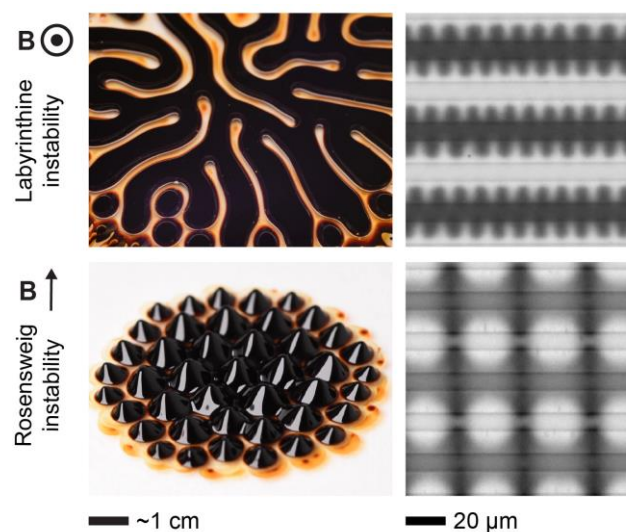
## Electrically Controllable Ferrofluids

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Ferrofluids are well known for their strong magnetic responsiveness. However, their response to electric fields is often not strong or studied at all. Here we show that it is possible to prepare strongly electrically responsive ferrofluids (“electroferrofluids”) by inducing a small but non-vanishing electric charge on iron oxide nanoparticles dispersed in a nonpolar solvent by using charge-carrying reverse micelles.[1] Application of electric field leads to electrophoretic motion of the charged nanoparticles and formation of steady-state dissipative nanoparticle concentration gradients. Because the nanoparticles are superparamagnetic, this translates to voltage-controlled local magnetic susceptibility and saturation magnetization. The magnetic nanoparticle gradients respond to magnetic fields analogously to the well-studied ferrofluid free surfaces. As a demonstration of this, we show that the gradients exhibit instabilities and pattern formation in magnetic field that resemble the classic labyrinthine instability and the normal-field instability (Fig. 1).



**Figure 1.** Photographs and micrographs showing the labyrinthine and normal-field instabilities exhibited by the electroferrofluid. Left column: macroscopic patterns driven by a magnetic field in presence of a free surface (ferrofluid-air interface). Right column: analogous microscopic patterns driven by a combination of electric and magnetic fields in absence of a free interface.

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# ORAL PRESENTATIONS

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Environmental Applications



# Ionic wind generation from magnetic fluid in various configurations

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In this study, a single dielectric barrier discharge (DBD) plasma actuator using magnetic fluid (MF), termed “MF-DBD plasma actuator”, is proposed and developed for generating an ionic wind. An MF filter aided with nonthermal plasma (NTP) has been developed [1]. The MF filter with NTP can collect low-resistive particulate matters, such as diesel particulate by electrostatic force without re-entrainment. The MF-DBD plasma actuator can be applied to the MF filter with NTP to establish a fanless air purification device. The mechanism of ionic wind generation in the MF-DBD plasma actuator is discussed based on the mechanism in conventional DBD plasma actuators. In this study, ionic wind generation from magnetic fluid in various configurations of electrode and magnetic fluid is of interest. Ionic wind, temperature distribution, ozone, and ion concentrations are investigated to obtain the fundamental characteristics of the MF-DBD plasma actuator. Consequently, the positive values of the discharge voltage and current are greater than the negative absolute values. This phenomenon can be explained using the ionic wind generation mechanism. A spike movement on the MF surface is observed. Based on the temperature analysis, natural convection occurs inside the MF, and convection suppresses the temperature increase of the MF by self-cooling. The characteristics of ion wind velocity and ozone concentration are clarified in various configurations of electrode and magnetic fluid.



Fig. 1 Photograph of MF-DBD plasma actuator

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# Iron Oxide and Metal Ferrite Nanocatalysts: Insights into the Generation of Free Radicals

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Magnetic iron oxide nanoparticles (MNPs) are able to act as catalytic agents in Fenton and Haber-Weiss reactions. The peroxidase-like activity at the surface of the MNPs results in the decomposition of H<sub>2</sub>O<sub>2</sub> into highly oxidative reactive oxygen species (ROS) such as hydroxyl (•OH) and hydroperoxyl radicals (•OOH) [1]. Depending on the MNPs nature, coating and oxidation state, it is possible to induce the generation of one or another free radical. In this work, ROS production with iron oxide (Fe<sub>3</sub>O<sub>4</sub>) and metal ferrite (MFe<sub>2</sub>O<sub>4</sub>, M= Co, Mn, Zn) nanoparticles was analyzed through electron paramagnetic resonance (EPR) and in the degradation process of acid orange 8 (AO8) as a model compound. Different sized MNPs (8 and 15 nm) were synthesized by a highly reproducible microwave-assisted procedure in polyol [2]. Selected samples underwent an oxidation treatment to form maghemite nanoparticles (γ-Fe<sub>2</sub>O<sub>3</sub>). As prepared samples were stable in aqueous suspensions thanks to polyol rests, while one was stabilized with citric acid (CA).

EPR assays (Figure 1) proved that ROS production increases when decreasing particle size due to a larger surface area. The nature of the metal ferrite can increase the •OH or •OOH depending on the doped metal. For example, MnFe<sub>2</sub>O<sub>4</sub> exhibited higher amount of •OOH than γ-Fe<sub>2</sub>O<sub>3</sub>, non-oxidized Fe<sub>3</sub>O<sub>4</sub> showed the greatest concentration of •OH, and the presence of Zn reduced significantly ROS production. Lastly, citric acid coating reduced the amount of ROS produced in comparison to polyol coated MNPs.

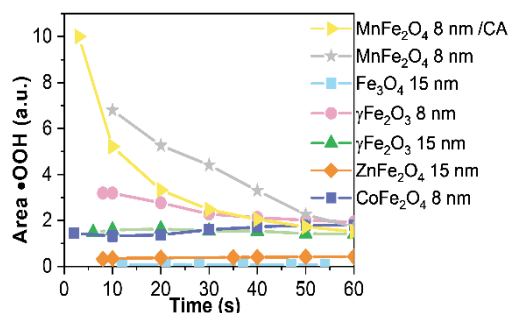
The reactivity of the radicals produced by MnFe<sub>2</sub>O<sub>4</sub> (•OOH) compared to the ones produced by Fe<sub>3</sub>O<sub>4</sub> (•OH) was tested by degrading AO8 aqueous solutions (100 ppm) in the presence of H<sub>2</sub>O<sub>2</sub> (0.3 M). Both radicals were able to successfully decompose the organic matter, but with the •OH radicals in a much faster manner. In general, MNPs reactivity can be tuned considering the size, doping and coating leading to efficient nanocatalysts for environmental remediation.

## Acknowledgments

This work was funded by EU commission, Project Ref: 101007629-NESTOR.

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**Figure 1.** Hydroperoxyl radical kinetics represented as the area of •OOH signal in the EPR spectra vs. time.

# Multifunctional Magnetic Nanocolloids for Hybrid Solar-Thermoelectric Energy Harvesting

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In the current pursuit to improve the energy conversion, production and storage efficiency of renewable technologies, hybridization (i.e. combining different energy production technologies in a single system) is considered a promising approach. Conventional low-mid temperature STCs consist of a dark surface devoted to sunlight absorption and to heat exchange with a thermal fluid. These systems are known to suffer from efficiency limitations due to the thermal resistance at the absorber-fluid interface. A substantial improvement can be expected by the nanofluid-based direct-absorption solar collector (NF-DASC) scheme, with nanofluid working both as a volumetric light absorber and a heat exchanger. Recently, ferrofluids have been tested in a DASC solar collector<sup>1</sup>. Interestingly, large thermoelectric effects are reported in similar types of ferrofluids<sup>2-5</sup> with corresponding Seebeck coefficient values above 1 mV/K, an order of magnitude higher than that of semiconductor counterparts. In this work, we report the first experimental investigation on the thermoelectric and the optical properties of stable aqueous ferrofluids containing maghemite nanoparticles. These nanoparticles are found to be an excellent solar radiation absorber and simultaneously a thermoelectric power-output enhancer with only a very small volume fraction. Combined together, ferrofluids open a new R&D opportunity to co-generate heat (through DASC) and electricity (through TE conversion) in hybrid solar thermal collectors for co-generating heat and power<sup>6</sup>.

## Acknowledgments

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# ORAL PRESENTATIONS

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Heat and Mass Transfer



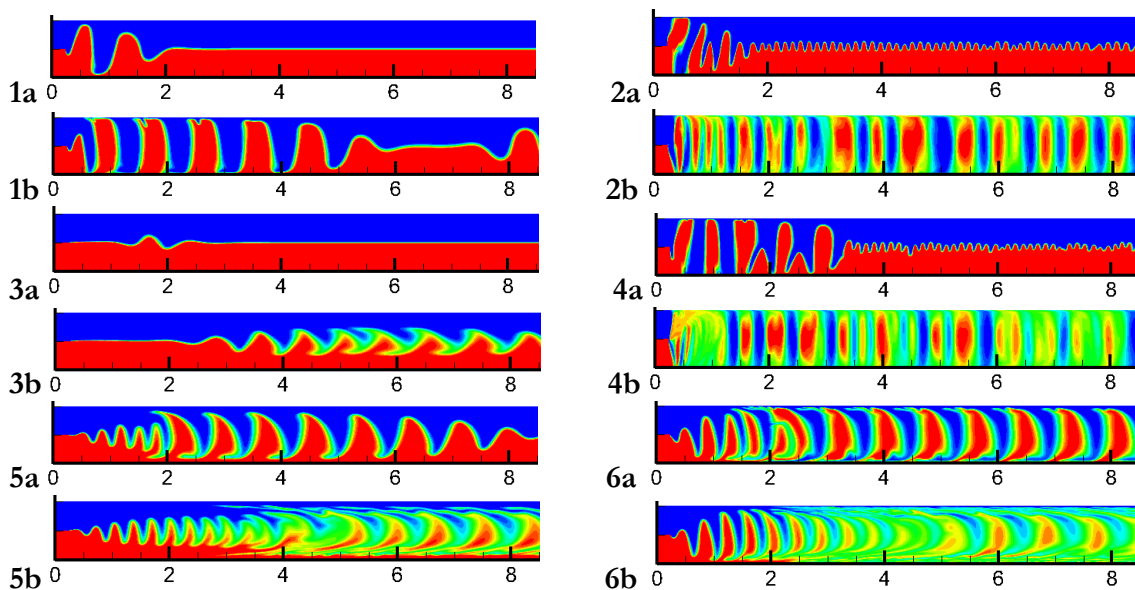
# Instability of the miscible magnetic/nonmagnetic fluids flow interface.

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One of the main problems of microfluidics is the mixing of fluids at low Reynolds numbers. If one of the fluids is magnetic, then the flow can be affected by a magnetic field [1]. If the magnetic field is normal to the interface of immobile magnetic/nonmagnetic fluids, then the interface is unstable [2], which can contribute to the intensification of fluid mixing. In this paper, we numerically study the behaviour of the interface between moving magnetic and nonmagnetic fluids with equal flow rates in a 2D plane channel. In addition to the instability mechanism discovered in [2], the source of disturbances and wave formation was found to be the point of confluence of two flows. The influence of the magnetic field and flow velocity on the amplitude, shape, phase and group velocities of waves at the interface has been studied. It is shown that two mechanisms of interface instability are competing (Fig.1).



**Fig. 1.** Waves and mixing.  $Re = uL\rho/\eta$ : **1,2** -0.0108; **3,4** - 0.108; **5,6** - 1.08.  $N_H = \mu_0 M_S H L / u_0 \eta$ : **1** -  $1.57 \cdot 10^5$ ; **2** -  $7.85 \cdot 10^5$ ; **3** -  $1.57 \cdot 10^4$ ; **4** -  $2.36 \cdot 10^5$ ; **5** -  $1.10 \cdot 10^4$ ; **6** -  $2.36 \cdot 10^4$ ; **a, b** - flow patterns at different times.

## Acknowledgments

Research has been funded by Grant No 20212019 from Program of Scientific Researches.

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# **Investigation of Heat Transfer Characteristics of the Self Driven Temperature-Sensitive Magnetic Fluid through a Nonmagnetic Porous in a Circular Tube**

Zhongwu Rong,<sup>†</sup> Yuhiro Iwamoto,<sup>†</sup> Yasushi Ido<sup>†</sup>, Atsuki Mitani,<sup>‡</sup> Ryohei Kobayashi,<sup>‡</sup>

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## **General specifications**

Temperature-sensitive magnetic fluid (TSMF) has a temperature-sensitive magnetization characteristic: the magnetization changes significantly when temperature changes because ferromagnetic particles with low Curie temperature are stably dispersed in the solvent [1]. Based on this characteristic, Iwamoto, et al. have reported a long-distance heat transfer device [2]. Because this fluid is driven by a magnetic field and temperature difference (i.e., called self-driven), the resulting flow phenomenon is very complex. In the previous study [3], we found that the self-driven heat flow of the TSMF in a single tube shows that the velocity near the heated wall is the largest. When the heat transfer area in the pipe can be increased, the driving force can also be greatly increased. This study focuses on porous materials, which have practicality and are expected to improve heat transfer.

In this study, the experimental apparatus is a closed-loop structure consisting of a Teflon tube with a path length of 2000 mm, and a heated alumina pipe. The TSMF TC3030S manufactured by Ferrotec Holdings Concept is used as the test fluid. The heating section consists mainly of a heating element, a double-layer heater, and an insulator. The heating element is an alumina pipe with a length of 40 mm, and an inner diameter of 2 mm. The non-magnetic porous aluminum material used in this study has a diameter of 2 mm and a porosity of 80%. The three experimental conditions were no porous material and lengths of porous material for 10 mm and 30 mm. The results show that the 10 mm porous material promotes self-driven heat transfer. The 30 mm porous material reduced heat transfer because of the presence of areas away from the magnetic field.

## **Acknowledgments**

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# Experimental investigation on magnetic fluid pool boiling heat transfer on hydrophilic surface

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## Abstract

According to past literature, there are many factors affecting pool boiling heat transfer, such as the working fluid [1,3,4], heated wall surface [1,2,4], etc. This work conducted an experimental study on the magnetic fluid pool boiling heat transfer on hydrophilic surface under an applied magnetic field, as shown in Figure 1. The heating section was heated by a copper rod with thermal conductivity of 401 W/m\*K, and Neodymium-iron-boron (Nd<sub>2</sub>Fe<sub>14</sub>B) permanent magnets were added in the section, and the condensation section was maintained at 40°C. The working fluid was maintained at a fixed saturation pressure of 12.35 kPa, and the metal surface in the boiling chamber used for the experiments was modified to be hydrophilic. The main purpose of the experiments was to study the pool boiling heat transfer performance considering a Fe<sub>3</sub>O<sub>4</sub> magnetic fluid on hydrophilic surface under a permanent magnetic field. The results showed that the applied magnetic field and hydrophilic surface could reduce the surface superheat temperature and enhance the heat transfer rate due to the changes in the surface condition.



Fig1. Experiment setting.

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# ORAL PRESENTATIONS

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Life and Science Applications



# Synthesis, Characterization and Cellular Internalization of Anisotropic Magnetic Nanoparticles

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Magnetic nanoparticles (MNPs) with elongated shape such as nanorods are of great interest for bio-applications as they notably exhibit higher heating efficiencies and a prolonged retention in tumour sites than their spherical counterparts [1]. The main issue during cells internalization is to avoid endosomal entrapment of nanoparticles, which prevent them from interacting with intracellular components and decrease their heating efficiency. Membrane translocation phenomena have already been observed with some anisotropic nanoparticles. Such process allows the internalization of these objects directly in the cytoplasm, without being trapped in endosomes [2].

In this study, a two-step robust synthesis method was optimized to produce magnetic nanorods of controlled composition in a large range of lengths and diameters. Water-soluble magnetite nanorods with high aspect ratios were obtained and then coated with a fluorescent silica shell. Core-shell magnetic nanorods were subsequently functionalized either with polyethylene glycol (PEG) or with zwitterionic molecules due to their antifouling properties. The cellular internalization of these elongated MNPs and of spherical core-shell MNPs [3] was thoroughly studied by confocal microscopy. At 4°C when endocytosis is blocked, internalization of elongated nanoparticles is still observed whereas that of spherical nanoparticles is no longer observed, confirming that the shape is a determining factor in the internalization of nanoparticles. Those first results confirmed a difference in the behaviour of elongated MNPs, suggesting passive diffusion, that transmission electron microscopy observations have been elucidated by showing the mechanisms involved in nanorods internalization.

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# Magnetic Nanoclusters to Increase the Sensitivity of a Lateral Flow Immunoassay to detect Pneumococcal Pneumonia

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Pneumonia is the leading cause of death from infectious diseases globally, significantly affecting the elderly and children [1]. It is the latter's leading cause of mortality after the neonatal period. Different agents can cause this illness, whose identification is essential to guide the proper treatment. *Streptococcus pneumoniae* bacteria is the leading pathogen responsible for most community-acquired pneumonia and other respiratory and systemic infections. Its diagnosis still needs to be improved, as the samples are difficult to obtain, take time and need sophisticated equipment usually centralized in a laboratory.

This work shows the development of a rapid diagnostic test to detect pneumolysin (PLY). This protein is an ideal diagnostic target found in handy samples: urine. PLY quantification was developed via a combination of magnetic labelling in a lateral flow immunoassay and an inductive sensor. The labels obtained by a polyol method are iron oxide nanoparticles of about 8 nm that are spherically clustered together with mean sizes of 89 nm. The polyacrylic acid on their surface enables their biofunctionalization with a monoclonal antibody for the specific recognition of the PLY. Different standard PLY solutions were used to calibrate the lateral flow test, which was read out dually: magnetic, with the inductive sensor, and optical, by image analysis with a phone camera. Both methods showed remarkable figures of merit, although the inductive reader yielded a larger linear range and better correlation factor, limit of detection, and limit of quantification. Finally, we proved the ability of the nanoclusters to concentrate diluted samples thanks to their magnetic character. Thanks to this simple technique, we considerably improved the limit of detection for both the inductive and optical sensors at 0.2 ng/mL and 0.6 ng/mL, respectively.

## Acknowledgments

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# **Combined effect of chemotherapy and photothermia based on the use of biomimetic magnetic nanoparticles functionalized with a ChoK $\alpha$ 1 inhibitor**

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Cancer is a disease with an enormous social and economic cost that causes a high number of deaths each year. Therefore, it would be important to improve the use of drugs already known to exert their effects on certain therapeutic targets, avoiding the possible side effects. Choline kinase  $\alpha$ 1 (ChoK $\alpha$ 1) is overexpressed in many types of cancers leading to a deregulated phosphatidylcholine metabolism associated with tumor progression. Thus, ChoK $\alpha$ 1 has become an attractive target for novel anticancer therapies. In this context, a new ChoK $\alpha$ 1 inhibitor named PL48 has emerged which exhibits enhanced lipophilicity due to possessing sulfur atoms in the bis-cationic head linker, in addition to free electron pairs on these atoms that allow establishing new interactions within the choline binding pocket of ChoK $\alpha$ 1, thus improving its affinity for the enzyme.

On the other hand, biomimetic magnetic nanoparticles (BMNP) are a novel carrier system for chemotherapeutic agents based on their magnetic properties, their innovative surface properties determined by the MamC protein, their biocompatibility and their ability as photothermia agents after laser exposure. The functionalization of BMNP with the ChoK $\alpha$ 1 inhibitor PL48 could provide a targeted and effective therapeutic system, with the possibility of combined treatments to fight cancer. Here we show the cytotoxicity effect of the nanoassembly BMNP-ChoK $\alpha$ 1 inhibitor on cancer cell lines when laser exposure is applied, serving a potential combined therapy against the cancer.

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# Temperature-responsive magnetic nano drug carriers for efficient treatment of pancreatic cancer

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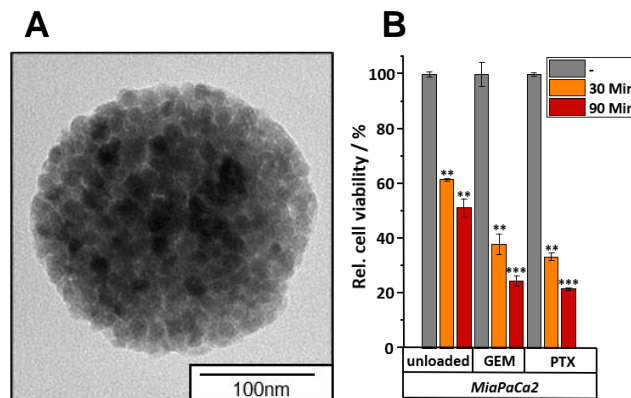
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Pancreatic tumour has a high probability of early metastasis. Conventional treatment is based on systemic chemotherapy, however, with a 5-year survival rate of 11 % and severe side effects for the patient. For an effective chemotherapy, a higher dose at the tumour site must be achieved. This can be realized by targeted drug delivery with magnetic carriers. An example are biodegradable thermos-responsive poly-(lactide-co-glycolide) acid (PLGA) nanospheres loaded with cytostatic drugs and magnetic nanoparticles (MNP). Local drug release is achieved by applying alternating magnetic fields to excite the MNP and generate heat and, in this way, induce the degradation of the PLGA nanosphere. In addition to an increase in local concentration of drugs, the local heat leads to a higher therapeutic efficiency due to the cancer cell's sensitivity to heat stress and increased intratumoral diffusion of drugs. In this work, the temperature-dependent drug release from PLGA nanospheres is tested with pancreatic tumor cells. For this, thermo-responsive magnetic PLGA nanospheres (Figure A) were synthesized. The PLGA nanospheres were loaded with cytostatic drugs (Gemcitabine or nAb-Paclitaxel) and MNP and incubated for 24 h with MIA PaCa-2 cells. The internalization kinetics of the magnetic PLGA nanospheres inside pancreatic cancer cells was tracked via transmission electron microscopy (TEM). The cells were exposed to an alternating magnetic field for different time intervals  $t = (0, 30, 90)$  min and heated up to a temperature of 43.6 °C. The cell viability was determined 24 h after treatment. Both, solely local heat generation and the combination with drug release, have a significant effect on cell viability (Figure B). The combinational therapy, however, has considerably more impact.



# Biocompatible folate targeted cobalt ferrite nanoparticles for magnetic hyperthermia

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The capability of magnetic nanoparticles (NPs) to release heat in alternating magnetic field, i.e., magnetic hyperthermia, is a very interesting property for medical application. Here we report the effect of cobalt content on magnetic properties and hyperthermic efficiency of spinel ferrites with various composition. Eight  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  samples were synthesized by alkaline coprecipitation with  $x=0-1$  cobalt content. The average size determined by light scattering was  $\sim 45$  nm for magnetite, while Co-ferrites showed larger hydrodynamic diameter (65-160 nm). The pH-dependent surface charging characterized by electrophoretic light scattering revealed, that pure magnetite has an IEP about  $\text{pH}\sim 8$ , but with increasing Co-content the  $\text{pH}_{\text{IEP}}$  shifted to more acidic values  $\sim 6.5$ . Based on magnetic measurements performed by SQUID at 5 and 300 K and calorimetric studies carried out at various frequencies (252-808 kHz) and at different field strengths (50-300 G) three samples (the pure MNP and Co-ferrite and one sample with 25 % theoretical cobalt content) were chosen to coat with a new PEG containing polysaccharide type copolymer anchored with folate side chain. Magnetization measurements and hyperthermia tests showed that the presence of the polymer layer on the particle's surface do not change their characteristics significantly, only a slight decrease in saturation magnetization and SAR values were observed. Although a moderate reduction was detected in viability for 48 h incubation for each bare nanoparticles in the case of all 4 cancer cell lines (human colon cancer (HCT116), human breast adenocarcinoma (MCF7), human normal bronchial epithelial (16HBE) and human dermal fibroblast (HDFa)) used, the reduced viability could not be observed for FA-INU-PEG coated samples, the values did not change neither after 24 h nor 48 hours.

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# Taking advantage of the magnetic functionality of nanostructures for induced movement

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The incorporation of magnetic nanostructures into a nano/micromotor design is a very convenient strategy for magnetic actuation. Accordingly, herein, some advantages with which nanostructures become endorsed when including magnetic nanoparticles in the final assembly, will be detailed. On one hand, we can consider the basic physical mechanism by which a magnetic field can be used to generate motion in fluidic environments, namely by inducing the so-called magnetophoretic motion by applying forces due to the magnetic field gradients, which require a spatially inhomogeneous field. Furthermore, this effect can be exploited jointly with self-propulsion of swimmers, such that, the movement becomes directed. On the other hand, we can also take into account the ability of magnetic nanoparticles to deliver heat, via the external stimulation using an alternating magnetic field. This heat delivered can have a tremendous impact in the induced movement, as it can be employed to catalyse the reactions involved in the concentration gradient generating the movement or to change the surrounding environment.

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# Optical or magnetic activation of iron oxide nanoparticles inside cells? The question behind thermal losses in biological environments

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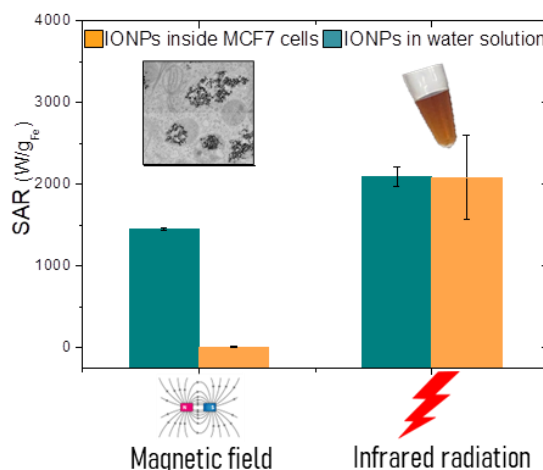
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Optical activation of heat losses mediated by iron oxide nanoparticles (IONPs) is gaining lots of interest. This is due to the high biocompatibility and biodegradability of IONPs, and their excellent photostability and photoconversion capacity. [1] Indeed, the use of IONPs for photothermal therapy (PTT) is an appealing option for the treatment of cancerous tissues. In this regard, the capacity of the IONPs-mediated thermal stress to kill cancer cells requires the preservation of the nanoparticle heating capacity in biological environments.[2] In this work, we report on the comparison of optical and magnetic heat losses released by IONPs of different size and shape in water solutions and inside living cells. For this study, we have employed cancer cell lines (HCT116 and MCF7), which were incubated with the IONPs (50-100  $\mu\text{gFe/mL}$ ) for different times. After 2-24 hours, cells were washed and detached, and cell pellets were irradiated (808 nm, 0.3-1  $\text{W/cm}^2$ ) or subjected to AC magnetic fields (100 kHz, 24 kA/m). Precise iron concentration in cell pellets was analysed by ICP-OES to perform comparison of heat losses mediated by IONPs dispersed in water solutions and inside cells under similar irradiation or magnetic field conditions. Optical spectroscopy analysis in the NIR range (700-900 nm) have revealed that aggregation of IONPs inside cells benefits optical heating, contrary to magnetic activation. Interestingly, such optical heating losses of IONPs in the range of mild hyperthermia (40-43°C) shrink cancer cell viability. The preservation of IONP photothermal properties inside cells entails great advantages for biomedical purposes in cancer treatment.



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# Targetable thermomagneto-phoretic nanopump for controlled release of biomolecules

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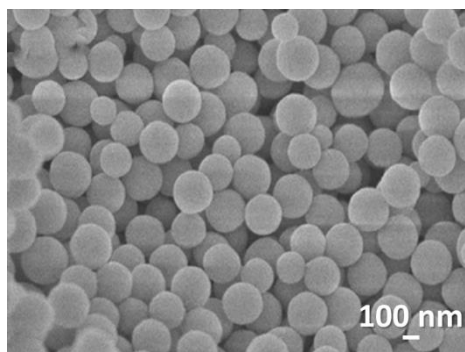
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Despite their approval for human use, nanoparticles of ferrimagnetic iron oxides - namely maghemite ( $\text{-Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) - often underperform for drug release and hyperthermia, thus requiring higher doses. This is partly due to the magnitude of their magnetic moment as well as their magnetic anisotropy [1].

We have designed a thermomagneto-phoretic nanopump for controlled drug release. This nanopump consists of several layers, namely: (i) a core consisting of a controlled aggregate of  $\text{Fe}_{20}\text{Ni}_{80}$  nanoparticles coated with a chelator that prevents Ni desorption; (ii) a layer of amorphous silica for the containment of the aggregates – either in liquid suspension or compacted, as needed -; (iii) a layer of poly(lactic-co-glycolic acid) (PLGA), a thermosensitive polymer with shape memory that retain and release the biomolecules of interest; (iv) optional surface linkers to facilitate the bonding of targeting biomolecules. By applying an external magnetic field, the core aggregates generate a thermophoretic effect that leads to a progressive, controlled PLGA destructuring and hence to the controlled release of the inner biomolecules.



**Figure 1:** SEM image of the  $\text{Fe}_{20}\text{Ni}_{80}@SiO_2@PLGA$  thermomagneto-phoretic nanopumps

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# Graphene-coated Fe nanoparticle suspensions for Safe and Steady Drug Delivery

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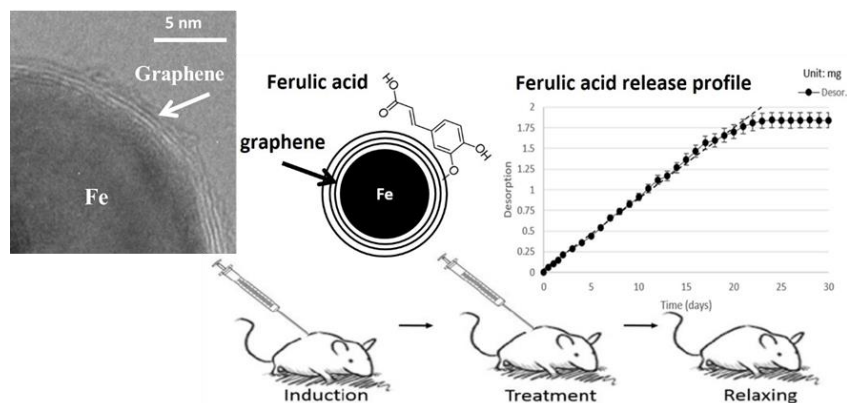
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New therapies demand drug delivery systems with added functionalities and proven safety, stability, and biocompatibility to achieve effective drug delivery and uptake. Herein, a magnetic nanovector (Fe@C) designed by encapsulating iron nanoparticles within a shell of 3-10 concentric graphene layers. These coating, exhaustively characterized through a wide range of techniques, serves as an impervious barrier, mitigating toxicity and enhancing the biocompatibility of the Fe@C suspension. Nanoparticle internalization, subcellular behavior, biocompatibility, and influence on cell viability and proliferation were investigated. Studies on human lung and skin cells indicate Fe@C is less toxic and more biocompatible than the magnetite nanoparticles coated by an amorphous carbon (Fe<sub>3</sub>O<sub>4</sub>@C), a popular drug carrier. As advanced HR-TEM and Raman spectroscopy suggest, Fe<sub>3</sub>O<sub>4</sub>@C exhibited more signs of degradation than Fe@C when exposed to murine macrophages. Unlike Fe<sub>3</sub>O<sub>4</sub>@C, Fe@C has a high drug loading capacity (0.18 g/g) for ferulic acid, an active pharmaceutical ingredient for diabetes treatment, and releases the drug at a constant dosing rate of 8.75 mg/g/day over 30 days. Ferulic acid released by Fe@C injected subcutaneously in diabetic BALB/c mice is effective in lowering the blood glucose level [1]



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## Magnetic hyperthermia of *M. blakemorei*

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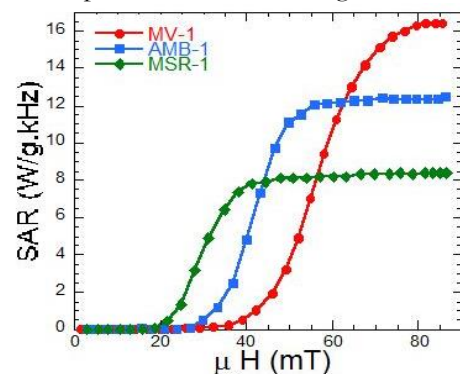
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Magnetotactic bacteria (MTB) are microorganisms able to align along the geomagnetic field lines due to their ability to biomineralize intracellular magnetic nanoparticles, called magnetosomes, that organize forming a chain. The morphology, composition and size of the magnetosomes are characteristic of each species and define the magnetic response of MTB and their potential use as nanorobots for cancer therapies such as magnetic hyperthermia. In this work, we study the suitability of the *Magnetovibrio blakemorei* (MV-1) species as a magnetic hyperthermia agent. The MV-1 bacteria synthesize elongated magnetite magnetosomes with truncated hexa-octahedral morphology (~35x35x53 nm<sup>3</sup>). In order to reveal any relationship between magnetosomes morphology and heating efficiency of MV-1 bacteria, we used different MTB species with other magnetosomes

morphology: *Magnetospirillum gryphiswaldense* (MSR-1) [1] and *Magnetospirillum magneticum* (AMB-1) [2]. MSR-1 and AMB-1 bacteria synthesize magnetite magnetosomes with a truncated octahedral morphology (~40nm) with a slight distortion. The main difference between both species lies in the arrangement of the magnetosomes in the chain: while MSR-1 present a full chain, AMB-1 presents a fragmented one. We evaluated the heating capacity of MV-1 by measuring the specific absorption rate (SAR) using a homemade AC magnetometer [3]. The SAR values were obtained from the area of the AC hysteresis loops measured at a frequency of 132 kHz and with magnetic field amplitudes ranging from 0 to 90mT. The evolution of SAR/f as a function of the applied field amplitude is depicted in Fig.1 within the values of MSR-1 and AMB-1 for comparison. The same trend is observed for the three species: at low field the SAR/f values are negligible, whereas above a threshold field SAR/f exhibits a rapid increase reaching saturation at 40, 53 and 80 mT with saturation values of 8, 12 and 16.4 W/gkHz for MSR-1, AMB-1 and MV-1, respectively. The main difference observed should be related to the different morphology of the magnetosomes: while MV-1 synthesize truncated hexa-octahedral, AMB-1 and MSR-1 synthesize truncated octahedral magnetic crystals with a slight distortion.



**Fig. 1:** Specific absorption rate normalized by frequency as a function of the magnetic field amplitude for MV-1, AMB-1 and MSR-1 species.

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# Study of cellular internalization of biomimetic nanoparticles in magnetic and photo induced hyperthermia treatments.

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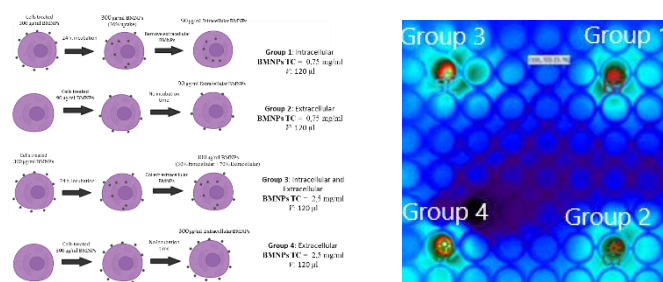
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Biomimetic magnetic nanoparticles (BMNPs) are an innovative tool to treat cancer since they behave as heating agents under laser irradiation (NIR), a technique called photothermia [1, 2]. However, it is still unclear whether, for the therapy to be efficient, BMNPs must be internalized by cells.

In this work, three different BMNP cellular uptake scenarios (intracellular BMNPs, extracellular BMNPs and intra + extracellular BMNPs) have been simulated and human hepatoblastoma (HepG2) cell viability was studied with BMNP suspensions after applying photothermia (Fig. 1).

As a result, it was observed that HepG2 cells containing only intracellular BMNPs show 26% cell viability after photothermia treatment, while those containing only extracellular BMNPs (at identical concentration) show 93% cell viability. When the amount of Fe is increased (BMNP concentration = 2.5 mg/mL) the viability of HepG2 cells after laser exposure decreases to 10% for the group of intra+extracellular group and 29% the extracellular group.

These results suggest that cellular internalization of nanoparticles is a very important factor to be taken into account in photothermal treatments. The greater the cellular uptake of MNP, the greater the desired effect.



**Figure 2.** Schematic of the groups of BMNPs corresponding to the experiment (above). Thermal image of these groups (bottom).

## Acknowledgments

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# ORAL PRESENTATIONS

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Magneto-Polymer Composites





# Influence of Strain on the Dynamic Behaviour of Magnetorheological Elastomer

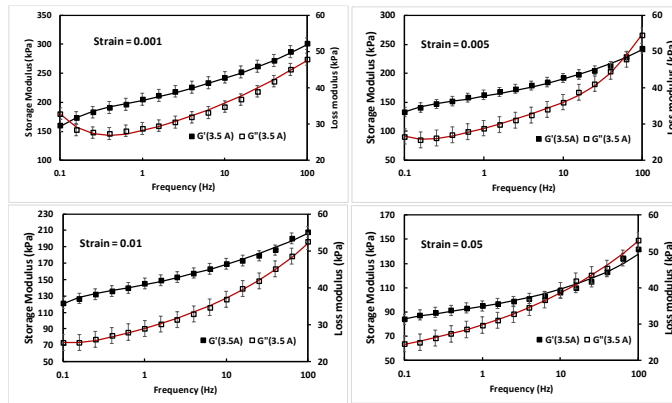
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Magnetorheological elastomer (MRE) is a composite polymer with tunable visco-elastic properties when exposed to the external magnetic field (H). These properties categorize this material as a «smart» material. The numerous applications of MRE, like seismic isolators, vibration absorbers, engine mounts, dampers, etc. High modulus and low Pyne effect factor are critical parameters in all these applications. These parameters are a function of (i) particle-matrix interaction, also known as interfacial interaction-defines the MRE's mechanical properties, (ii) particle magnetic properties, and (c) particle concentration. One way to improve particle-matrix interaction is to use different shapes or morphology of magnetic particles. More cross-points are available because of the shape, which enhances the resistance of the interfacial bond. These properties depend on applied strain amplitude and frequency in the dynamic mode. The main aim of the present work is to show the influence of strain amplitude in anisotropic particle-shaped based MRE at a different frequency. The dynamic behaviour is explained using a new fractional derivative Maxwell model, which accounts for the influence of strain and magnetic field in a wide range of frequencies (0.1Hz to 100 Hz). Anton-Paar MCR 301, attached with MRD 1T/180°C instrument, is used to study the dynamic rheology.



## Results & discussion

Figure 1 shows the influence of strain on moduli at a given magnetic field (current  $I = 3.5\text{A}$ ). The line fits the new modified fractional Maxwell model given by equation (1). Here,  $\Phi$ ,  $B$  and  $\gamma$  are particle volume fraction, magnetic field strength and strain amplitude, respectively. The first term on the right-hand side represents modulus

in zero fields,  $\Delta G^*$  is magnetic field induced modulus,  $f$  is frequency, and  $G_f(\gamma)$  is friction contribution to moduli which adds for loss modulus in total. This new model can capture low-frequency behaviour as well as strain influence in both moduli very well ( $R^2 > 99\%$ )

$$G^*(B, \gamma, f) = G^* + (\Delta G^*(\varphi, B, \gamma)) [f^n \mp G_f(\gamma)] \quad (1)$$

## Acknowledgement

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# Induced changes in shape and transport properties of magnetic gels and elastomers

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## Overview

Magnetic gels and elastomers contain magnetizable particles in soft elastic carrier media. We wish to understand how properties on the particle scale affect overall material behavior [1].

## Magnetostriction and actuation

First, we study how induced magnetic particle interactions determine the deformation of the whole system. Explicit analytical expressions allow us to calculate the overall distortion from the forces exerted by the discrete, individual magnetic particles and their spatial arrangement [2]. Understanding such relations is important to generate soft magnetoelastic actuators that show requested types of deformation. As an example, we suggest the construction of soft magnetoelastic twist actuators that feature torsional types of distortion [3, 4].

## Magnetically induced changes in thermal conductivity

Additionally, we study via bead-spring models how induced internal rearrangements of the particles modify the transport properties, specifically thermal [5] or electric conductivity. Variations occur with achieved magnetization, particle number and density.

## Perspective

Our analysis and observations are theoretical. We hope to stimulate by our results actual experimental investigations. Particularly this concerns the realization of specific types of actuator and the study of transport properties.

## Acknowledgments

We thank the German Research Foundation DFG for support through the Heisenberg Grant ME 3571/4 and the priority program SPP 1681, grant no. ME 3571/3.

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# Importance of the magnetic particles' functionalization in the design of ferrogels

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The correct functionalization of the magnetic particles is crucial it modulates the interaction between their surface and the polymeric filaments of the hydrogels, having a direct impact on their final properties [1]. In addition, magnetic particles with a suitable chemical surface can conjugate drugs, proteins, enzymes, or antibodies, which is required in many biomedical applications. However, in the most representative literature on magnetic hydrogels, magnetic particles are generally used as received, that is, without any functionalization. In addition, the surface of the particles can be used to create interactions with the fibers [2], which in turn can affect the final properties of the hydrogels and even provide more favorable characteristics, such as better adhesion of biological species (for example, cells). However, few attempts to chemically functionalize magnetic particles using groups apart from amines are found in the literature [2].

In this work [3] we determined the role played by the functionalization of the iron particle surface in the final properties of alginate ferrogels. For this aim, silica-covered iron microparticles were taken as a starting point. These control particles were further functionalized with different functional groups including hydroxyl, amine, glycidoxo, phenyl, and thiocyanate; being novel many of these modifications since they were presented in this work for the first time. The different functionalizations affected the chemical interaction between the hydrogel polymeric matrix and the surface of the iron particles in a different way, contributing to the appearance of diverse microstructures, mechanical properties and biocompatibility.

## Acknowledgments

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# Magnetic training of the soft magnetorheological elastomers

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The hysteresis of magnetization curves of magnetically soft magnetorheological elastomers has been previously observed experimentally [1]. The appearance of hysteresis is characteristic of samples with a sufficiently soft polymer matrix, which allows magnetically soft microparticles to move and be structured under the action of an external magnetic field. In [2] a physical model explaining the appearance of such hysteresis was proposed.

In this study, we consider the cyclic magnetization of soft matrix-based elastomers. It is shown how subsequent repeated magnetization affects the magnetic behavior of the composite: the consistently measured magnetization loops become narrower and their initial linear slope increases. The loops measured at later cycles demonstrate a higher magnetization of the composites at low magnetic fields compared with the very first initial loop, i.e. the magnetic susceptibility of the composite is increased. Moreover, the initial magnetization loops corresponding to different polarities of the applied field also differ from each other. Another distinctive feature of the magnetic behavior of composites with soft matrix which is influenced by the repeated magnetization is the local maxima of their differential susceptibility curves appearing at the low fields. Obtained results are related to irreversible changes in the microstructural state of the composites, which affects the magnetic macroscopic response of the material. After a certain number of magnetization cycles the composite sample becomes trained, i.e. significant irreversible microstructural changes no longer occur. The magnetization curves of the trained sample are therefore reproducible, irrespective of the polarity reversal of the magnetic field. We report the results of a systematic study of such magnetorheological elastomer training.

## Acknowledgments

Financial support by Deutsche Forschungsgemeinschaft (DFG) under Grant Bo 3343/3-1 is gratefully acknowledged.

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## Shape-morphing magnetoactive elastomers

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### Abstract

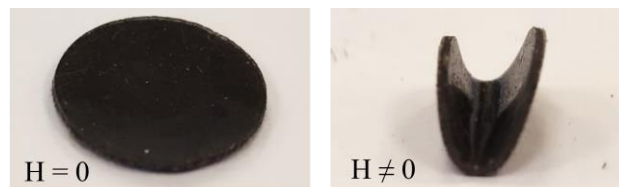
This work presents the development and characterization of a magnetoactive elastomeric material that exhibits high shape morphing under the application of a magnetic field. The elastomer comprises a silicon-based matrix reinforced with soft-magnetic Fe microparticles with 215 Am<sup>2</sup>/kg magnetic saturation. The internal composition of the material is non-uniform, featuring a multilayer arrangement, with the highest concentration of particles in one half of the thickness and highest concentration of matrix in the other half, resulting in a unique set of properties and behavior under magnetic fields.

The magnetoactive elastomers were manufactured in two distinct geometries: sheets and tubes. To create a layered distribution of the components, gravitational force was employed for the sheet format, which causes the particles to settle, and centrifugal force for the tube format, where multilayer distribution is achieved rotating the mold at high speeds.

To evaluate the material properties, the sheet format was employed during the experimental characterization, in which magnetorheological and deformation tests were carried out.

The study of the rheological properties revealed a significant change in the dynamic modulus of the magnetoactive elastomer when a magnetic field was applied, which is indicative of the high MR effect of the material.

Regarding the deformability of the elastomer, to monitor the displacements and curvatures generated under the action of a magnetic field, an optical, noninvasive and magnetic field-insensitive system based on 3D stereoscopic technique was employed. The results showed that the multilayer configuration elastomer displayed deformations of up to 23.7% when exposed to a 207 kA/m magnetic field. Moreover, the deformation level was linearly variable and controllable by the strength of the applied magnetic field, allowing for dynamic deformation of the material.



*Figure 3. Magnetoactive elastomer shape morphing response*

### Acknowledgments

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# Magneto-active composites: From microscopic structure to effective magnetization

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When magnetizable particles are embedded into an elastic polymer network, a field-controllable material known as magneto-active elastomer (MAE) is created. Such composites have gained great scientific interest due to their ability for versatile and remotely controllable modifications like magnetically induced deformations and actuation stresses, as well as anisotropic enhancement of mechanical moduli up to several orders of magnitude depending on strength and orientation of the external magnetic field. As a consequence, the application potentials are manifold, ranging from new energy harvesting technologies, integrated sensors, artificial muscles to soft robotics.

Due to strong magneto-mechanical coupling on short and long length scales a general characterization of the material behavior is very challenging. We recently developed a powerful model based on dipole interactions which illustrates various aspects of the intrinsic magneto-mechanical interplay. The formulation allows to account simultaneously for the underlying particle distribution and overall sample form. In this way, also an analytic approximation for the effective magnetization behavior in MAEs, spanning from linear to saturation regime, for isotropic and anisotropic particle arrangements is derived. The results clearly reveal that anisotropic particle distributions have an equivalent effect as anisometric sample shapes. Furthermore, our approach enables an efficient characterization of magnetization fields in real-sized magneto-active composites which can be implemented in macro-continuum models.

## **Acknowledgments**

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# Vibration-driven mobile robots based on multipole magnetoactive elastomers

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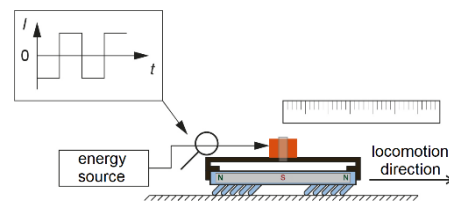
Magnetoactive elastomers (MAEs) consist of an elastic matrix containing micron-sized magnetically soft and/or hard particles. An external or internal magnetic field can modify mechanical and rheological properties of these materials. Specifically, the magnetization of MAEs containing magnetically hard particles by imposing a strong magnetic field after their polymerization enables to create elastic magnets.

Such intelligent materials offer great potential in the field of soft robotics. Motion systems based on MAE deformation excited by an alternating magnetic field are already realized with a minimal number of actuators. The peculiarity of the present work is the use of multipole MAEs for the vibration-driven unidimensional and planar locomotion. The functional element is synthesized of an MAE with both magnetically hard and soft particles and is permanently magnetized having two north poles at the ends and one south pole in the middle. The periodic transverse bending of the MAE element is induced by an external or integrated magnetic field source driven at different excitation frequencies. The system's directed motion is due to the cyclic interplay of inertia and asymmetric friction forces caused by silicone bristles protruding at an oblique angle from the underside of the MAE element.

The locomotion system with an integrated magnetic field source is shown in figure. Its design has an additively manufactured attachment, which mounts an electromagnetic coil in the center. In each actuation cycle, the current direction in the coil is changed from negative to positive, so that the south-poled middle part of the MAE element is attracted and then repelled from the coil. This magnetic forcing results in asymmetric bending vibrations of the MAE element around its straight configuration and its horizontal locomotion in the direction opposite to the inclination direction of the bristles. Our investigations show that the system can move on horizontal as well as inclined surfaces.

The strong resonant dependency of the advancing speed on the actuation frequency is observed. The system's characteristics like load carrying capacity and obstacles overcoming is examined.

The use of multipole magnetized MAEs in combination with simple design, as reported here, makes it possible to realize mobile robots with a single magnetic actuation deploying the principle of vibrational locomotion.



## Acknowledgments

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# **Thermoresponsive core/shell nanoparticles for chemotherapy and phototherapy against cancer**

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## **Introduction and objective**

Nanoformulations for control drug delivery and novel therapeutical approaches (i.e. photothermal therapy) offer a promising opportunity to enhance survival rate at late stages of cancer disease. The goal of this work was to engineer a biocompatible thermoresponsive magnetite (Fe<sub>3</sub>O<sub>4</sub>)/poly( $\epsilon$ -caprolactone) (PCL) core/shell nanoparticles (NPs) loaded with gemcitabine (Gem) with potential in controlled drug delivery and phototherapy against cancer.

## **Methods**

Fe<sub>3</sub>O<sub>4</sub> cores and Gem molecules were loaded into a PCL matrix following a previously reported procedure [1]. Resultant NPs were characterized by DLS, HR-TEM, and TGA and tested by an hemocompatibility assay. Drug loading (DL, %) and thermoresponsive character of the NPs was investigated following a dialysis bag method. Photothermal potential was investigated with a 808 nm laser.

## **Results and conclusions**

Fe<sub>3</sub>O<sub>4</sub>/PCL NPs were found to be  $\approx$  130 nm with a Fe<sub>3</sub>O<sub>4</sub> content of  $\approx$  75% and an adequate hemocompatibility profile. PCL shell possess an efficient Gem loading capacity (DL of  $\approx$  11%) with a potential thermoresponsive behavior ( $\approx$  twenty-fold faster Gem release at 45° compared to 37°, at pH 7.4). Antitumor photothermal potential (39-42°C) was observed from the lowest NPs concentration evaluated (0.1 mg/mL). Thus, Fe<sub>3</sub>O<sub>4</sub>/PCL core/shell NPs demonstrated a great potential as thermoresponsive core/shell nanoparticles for chemotherapy and phototherapy against cancer.

## **Acknowledgments**

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# Energy harvesting using permanent magnet elastomer

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Magnetorheological elastomers (MREs) are magnetic composite materials with a stable dispersion of magnetic particles in a viscoelastic material. MREs show unique behaviors such as magnetostriction, Pseud-Villari effect, and MR effect [1] under an external magnetic field. In conventional MREs, soft magnetic particles such as iron oxide are dispersed. Because the soft magnetic particles have low coercive force, an external magnetic field imposed by rigid electromagnetic coils or permanent magnets needs to induce the MREs' magnetic behaviors. This is a dilemma in the field of MREs. This study has proposed a permanent magnet elastomer (PME) in which neodymium particles (hard magnetic particles) are dispersed. Because neodymium has a high coercive force, once magnetized, PME keeps its magnetization and behaves as a permanent magnet. The magnetized NdFeB particles are able to move relatively freely, interacting with the polymer network. PME is a soft permanent magnet (see Fig. 1). Because of its softness, the ambient magnetic flux of the PME changes dramatically with mechanical deformation. This is associated with the motions of magnetized NdFeB particles in polymer matrices. By placing a pickup coil around the PME, electric power can be generated based on the principle of electromagnetic induction. It is expected to be possible to construct an energy harvesting system and battery-free wireless sensors for the IoT using PME. In the present study, we prepared a PME with a diameter of 18 mm and a height of 18 mm, investigated its power generation performance, and conducted a demonstration of a battery-free wireless sensor operation. As a result, 2.5 V of no-load open-circuit voltage could be achieved at a large stroke of 10 mm and very low frequency of 10 Hz, which could not be achieved with conventional energy harvestings such as piezoelectric elements and inversed magnetostriction materials. PME enables the realization of battery-free wireless sensors, and wireless data transmission of temperature sensors has been confirmed when PME energy harvesting is used as its power source.

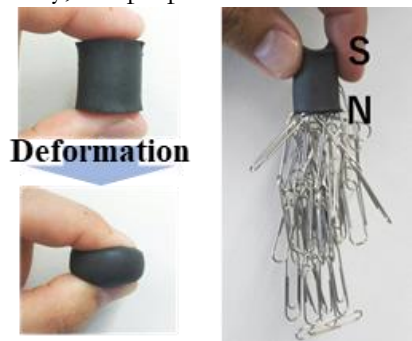


Fig. 1 Permanent magnet elastomer

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# ORAL PRESENTATIONS

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Rheology and Structures





# **Discontinuous Shear Thickening (DST) transition with spherical iron particles coated by adsorbed brush polymer**

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The phenomenon of discontinuous shear thickening (DST) is observed in suspensions of solid particles with a very high volume fraction. It is characterized, among other things, by a sudden increase in viscosity above a critical stress. This jump of viscosity can be reproduced in numerical simulations by introducing a transition from lubricated contacts between particles to frictional contacts above a given local force between particles. Using a suspension of magnetic particles at high volume fraction we have, for the first time, demonstrated experimentally the presence of a frictional network of particles by a simultaneous measurement of the electrical resistance of the suspension and of the rheological curve. Furthermore the application of a small magnetic field allows to trigger the DST transition opening the way to new applications of magnetorheological suspensions (MRS), in particular in the field of robotics. We shall emphasize the determining role of the superplasticizer molecule used to coat the particles in the DST transition induced by a magnetic field. In particular we shall show that the whole rheological behavior can be explained by the interpenetration of the polymer layers in the contact zone under the effect of the shear stress and of the magnetic stress followed by their expulsion above a stress threshold corresponding to the DST transition[1]. An obstacle for the applications of MRS remains the sedimentation and aggregation linked to the high density of the iron microparticles. We have found that a small fraction of ferromagnetic particles (about 5% in volume) within a concentrated suspension of calcium carbonate particles is not only sufficient to trigger the transition by application of a magnetic field but also optimum in terms of the amplitude of the jump in viscosity. We explain this result from geometric considerations on the insertion and structuration of small iron particles in a network of bigger non magnetic particles.

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## Multiaxial toggled field self-assembly

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Magnetorheological (MR) fluids of interest in current applications are prepared by dispersion of magnetisable particles in (non-magnetic) liquid carriers. They exhibit a remarkable rheological change (so-called MR effect) upon the application of a magnetic field. The reason for this is the magnetic field-guided colloidal assembly of the dispersed magnetisable particles [1].

The self-assembly of magnetic colloids can be controlled through the field configuration (DC, AC or combinations) [2]. Understanding the underlying physical mechanism is crucial to enhance magnetorheology and successfully answer fundamental questions such as whether a limiting MR effect exists. Additionally, finding new routes to speed up the directed self-assembly is a hot topic today [3] and toggled fields offer an easy route to lower-energy states as thermal motion during field-off periods enhances particle rearrangement [4].

In this communication, we describe the construction of a device that is capable of generating strong, multi-axial toggled magnetic fields. We also conduct carefully controlled experiments on magnetic latex particles at a wide range of field frequencies. Our results show that the aggregation process can be substantially accelerated (up to several orders of magnitude) by superimposing orthogonal magnetic pulses. Additionally, we observe the emergence of novel and exotic structures, such as circular and square aggregates.

A phase diagram is constructed by examining the dependence of the final structure on magnetic field frequency and strength in perpendicular directions. Furthermore, we identify a master curve that explains the evolution of the system's length scale.

### Acknowledgments

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# Interaction of aggregates in ferrofluids according to small-angle scattering data

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Problems of studying various interaction effects between aggregates in real ferrofluids with a stable aggregation phase are considered. Small-angle scattering of X-rays and neutrons is the most direct experimental method for evaluating correlations on a scale from  $\sim 1$  nm to  $\sim 100$  nm. Even in highly stable ferrofluids (e.g. magnetic particles with single coating by surfactants in organic solvents), the aggregation phase can exist in thermodynamic equilibrium with monomeric particles because of competing interactions: magnetic attraction and Brownian repulsion between particles. In some cases, despite the presence of colloidal (non-equilibrium) aggregation in ferrofluids based on a highly polar media (e.g. water), the systems remain stable in time. Compact colloidal clusters consisting of comparatively small number of particles in them are of current interest regarding some applications (e.g. magnetic hyperthermia) due to a specific behavior of magnetization different from that for purely superparamagnetic systems. In concentrated (but still stable) systems, a significant fraction of magnetic particles are in the aggregate state, which means that the clusters, interacting with each other in solution, start to contribute to the correlation effects reflected in small-angle scattering. This report is devoted to the analysis of these effects for concentrated water-based ferrofluids with double-layered surfactant (fatty acids) coating of magnetic nanoparticles [1].

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# ORAL PRESENTATIONS

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Technological Applications



# Reversible clustering and separation of magnetic particles in a microfluidic environment using engineered magnetic field landscapes

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For the implementation of future Lab-on-a-chip (LOC) devices or micro total analysis systems ( $\mu$ TAS), the controlled actuation of magnetic nano- and microparticles is considered to be highly advantageous since the manipulation can be achieved via magnetic fields without disturbing occurring microfluidic or biological processes [1]. Detection of an analyte species in these systems typically requires appropriately surface-functionalized particles that enable specific binding of the analyte to catcher molecules. An important task is then to separate and identify particles based on their analyte interaction. As a prototypical methodology, we present in this work the usage of engineered magnetic domain patterns within topographically flat magnetic thin film systems and the dynamic transformation of the emerging magnetic stray field landscape (MFL) via external magnetic field pulses.

First, we demonstrate a locally defined focusing of superparamagnetic microparticles (SPPs) within an aqueous medium using the MFL originating from parallel magnetic stripe domains of gradually decreasing/increasing length. Converging and diverging SPP motion trajectories were induced, allowing for a controlled formation and decomposition of closely packed particle clusters. As SPPs are brought into proximity to each other within these clusters, a potential route for analyte detection is opened up due to an inducible particle aggregation, with the analyte acting as molecular bridges between single particles [2]. Secondly, another domain pattern consisting of parallel stripe domains with gradually increasing width will be introduced for the separation of SPPs based on their magnetophoretic mobility. We show that SPPs can be immobilized at different locations above the chip substrate while applying a constant external magnetic field pulse sequence. For both investigated systems, it will be discussed how the observed behavior is determined by the acting forces and how it is influenced by the duration of the external field pulses.

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# **Magnetic tweezer optimization for multiplexed Microrheology measurements**

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Magnetic tweezers (MT) are devices able to apply forces to magnetic micro and nanoparticles immersed in a fluid by using permanent magnets or active electric coils. This magnetophoretic force is proportional to the magnetization of the particle ( $\mathbf{m}$ ) and to the gradient of the magnetic field strength ( $\mathbf{H}_0$ ). At low fields,  $\mathbf{m}$  is proportional to  $\mathbf{H}_0$ , and the magnetophoretic force relies not only on the gradient of the magnetic field but on its value as well.

MT can be doubly used either as force transducer or as a positioning system. Both capabilities require videomicroscopy devices to follow the trajectories of the particles and also a precise knowledge of the magnetic fields within the workspace. When magnetic fields are generated by coils, a precise spatiotemporal generation over the workspace can be performed by emplacing the coils in specific positions and controlling the voltage applied.

This accuracy on the force applied to a magnetic bead enhances the capabilities of the microrheology as the set of techniques for measuring local rheological properties, like microviscosity. This is due to the relationship between the speed of the tracked bead and the force applied in the position where the bead is placed. However, this force usually has very different values along the sample with higher values close to the magnetic actuators.

The main contribution is the optimization of the inner space of the MT by adding ferrites in specific locations. By doing this, the relationship between the magnetic field and its gradient is modified within the workspace in order to increase the applied force while maintaining its homogeneity along a wide region where many magnetic particles can be moved due to the same effort. This multiplexed measurement provides information of the force, position and speed of each particle that are randomly distributed along the sample. This optimization significantly increases the resolution of the parameter measured, like microviscosity, as well as the speed of the essays. However, a more complex filtering system is needed in order to exclude non-valid beads.

The optimized system of ferrites is removable and designed for a far-field magnetic field generator. So this, two different working modes are optimized: homogeneous field and homogeneous force. Results show a magnetophoretic force increment of 280% and a decrement of the relative force variation of 6.4%. The system is optimized for measurements within a circle of 800  $\mu\text{m}$  diameter.

## **Acknowledgments**

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# Magneto-dielectric properties of a bi-dispersed magnetic nanofluid

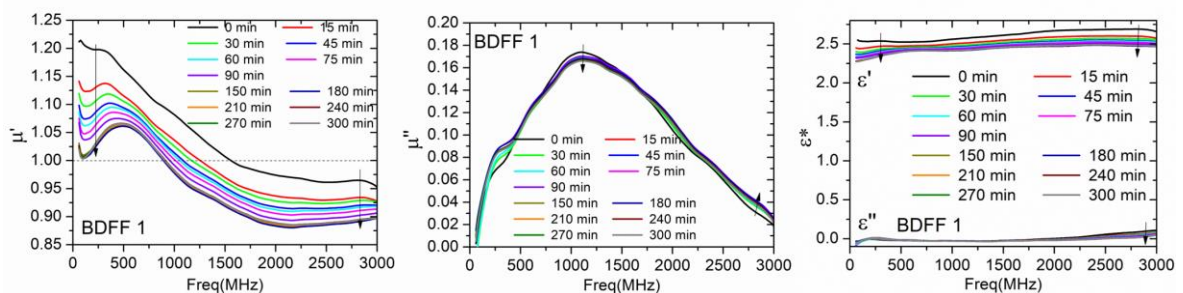
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The bi-dispersed magnetic fluid [1] is prepared by dispersing commercially purchased maghemite (micron-sized) particles in the laboratory-prepared kerosene-based magnetic nanofluid (magnetite in kerosene) and two such fluids are prepared with different concentration of micron-sized particles. The dielectric and magnetic properties of magnetic nanofluid, complex magnetic permeability ( $\mu^*$ ) and complex dielectric permittivity ( $\epsilon^*$ ), were studied as a function of frequency and external magnetic field in the broad frequency range [2]. It was shown that energy absorption occurs in the magnetic nanofluid due to phenomena called magnetic relaxation and ferromagnetic resonance. Here we have studied the dielectric and magnetic properties of bi-dispersed magnetic fluids as a function of time and concentration of micron-sized particles for the first time. The energy absorption enhances in the fluid due to the presence of micron-sized particles. As time progresses, these properties get modified significantly as shown in the figure. The  $\mu'$  and  $\epsilon'$  values decrease as time progresses in the whole frequency range. The  $\mu''$  maximum and  $\epsilon''$  values shift down by a small extent with time. It is challenging to keep micron-sized particles suspended in a liquid carrier. Our results indicate that here the micron-sized particles might get combined with other micron-sized particles and nanoparticles to form agglomerates. As time passes these agglomerates start to settle down, sedimentation takes place. As a result, the properties of the fluid get modified. In order to evaluate sedimentation in the bi-dispersed magnetic fluid, a simple set-up is used, where the inductance of a coil changes as the particles settle down to the bottom with time. It is confirmed from the experiment that sedimentation is less when the concentration of micron-sized particles is larger. The dielectric and magnetic properties at high frequencies are much more sensitive to the occurrence of agglomeration and sedimentation in the fluid.



## Acknowledgments

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# ORAL PRESENTATIONS

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Physical Properties





## Optimal size of iron oxide nanoflowers at 22 nm for magnetic hyperthermia

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Among different types of magnetic nanoparticles (MNPs) introduced so far for biomedical applications, iron oxide nanoflowers (IONFs) synthesized through a polyol route firstly introduced by Caruntu et al.<sup>[1]</sup> gained attention due to their remarkable magnetic properties. These NPs are characterized by a multi-core structure as observed by TEM, presumably created through mechanism of oriented aggregation of the nuclei formed by the iron oxide precursors, while they appear as mono-crystals in HR-TEM, as if the nuclei were sintered altogether by the growth process, performed in high boiling point polyol (220°C). This peculiarity is thought to be at the origin of their great efficacy in magnetic hyperthermia, making them competitive even with the largest natural MNPs called “magnetosomes”. This communication presents a library of monocoresh MNPs and multicore IONFs with narrow size dispersity, with diameters ranging from 11 to 30 nm. In-depth characterization of the synthesized MNPs was carried on, from their structural features (overall diameter, mono or multicore morphology, number and size of cores, crystal size and structural defects) to their magnetic properties probed under both static field (saturation magnetization, blocking temperature, anisotropy energy constant and magnetic domain size) and alternating magnetic field (AMF). The heating performances of the MNPs were investigated by AC magnetometry by determining the specific adsorption rate SAR ( $W \cdot g^{-1} \gamma\text{-Fe}_2\text{O}_3$ ) by direct measurement of the dynamic magnetization hysteresis loops using commercial pick-up coil instrument over a wide range of AMF conditions from 4 to 24  $kA \cdot m^{-1}$  and frequencies in the range 146–344 kHz.<sup>[2]</sup> This way, the SAR variation of all the synthesized batches with overall diameter (from TEM) as well as crystal size (from XRD) and magnetic domain size (from the fit of VSM curves) was evaluated under 24 different AMF conditions within a reasonable experimental time. These multi-parametric study shows that the SAR of MNPs varies not only with the size, structure and morphology of the NPs but also with the selected AMF conditions, according to theoretical predictions of Linear Response Theory (LRT) and Stoner-Wohlfarth (SW) models and joining numerical simulations reported by Mehdaoui et al.<sup>[3]</sup> and Engelmann et al.<sup>[4]</sup> for the variation of SAR with MNP diameters.

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# Monodispered $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoclusters based magnetic fluid: Synthesis and characterization

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Magnetic nanoclusters (nanoflowers) demonstrate unique physical and magnetic properties as compared to their constituent nanoparticles due to the intra-cluster interactions. This paper shows the synthesis and characterization of size tuning magnetic nanoclusters for different applications. The formation mechanism of the nanoclusters and the strategies to control the dimensions of the clusters are described in detail. The nanoclusters were characterized using XRD, TEM, DLS, VSM and SAXS. The size of nanoclusters was tuned from 107 to 228 nm using hydrothermal route by controlling the reaction time. The model is developed to fit the SAXS data to retrieve the size of the nanoclusters as well as its constituent particles. It is seen that the cluster size obtained from various techniques are complementary to each other. Figure 1 shows the SAXS pattern fitted with the model for a typical sample. This is a first attempt of its kind to show the size of nanoclusters determined from different techniques are comparable. The dispersion of nanoclusters can be used for various biomedical applications as well as for other applications where the large surface area to volume ratio is desirable.

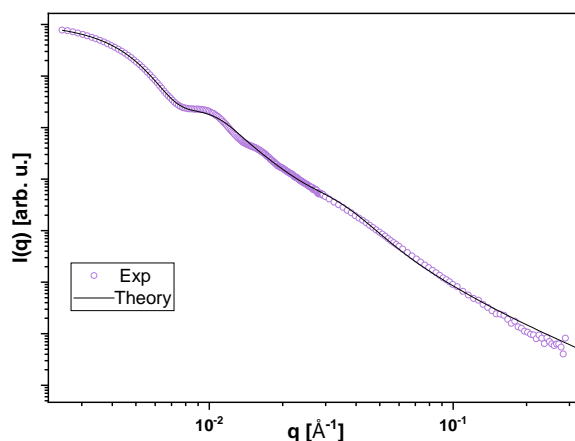


Figure 1: SAXS pattern (symbol) fitted with the model (line) for a typical sample.

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# Neutrons-useful tool for structural study of magnetic nanoparticles in magnetic fluids and their composites

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Possibility of neutron and X-ray scattering methods for structural investigations at nanoscale will be discussed in detail according to our huge experience over the last 10 years: Namely, results of neutron reflectometry (NR) [1] and small-angle neutron scattering (SANS) for nanoscale characterization of magnetic nanoparticles in bulk and at interfaces will be shown. Also basic principles of small-angle scattering and reflectometry techniques will be explained. The structural analysis of various types of magnetic fluids (MFs); MNPs with bio-macromolecules (magnetoferritin, amyloids, magnetosomes among others), textile-based nanocomposites [2] with MNPs and ferronematics (composite systems of liquid crystal (LC) with MNPs) will be described in details during the presentation. Additionally the interaction characteristics between surfactant/polymer molecules used in stabilization of MFs were investigated, which is very important for understanding the synthesis procedure of highly stable magnetic fluids with controllable properties. Also effect of external magnetic/electric fields on the behavior of MNPs will be presented according to the neutron scattering data. Neutron and X-ray scattering methods have been used to study the clustering of MNPs in a LC matrix, too especially on the alignment of MNPs in different phases of liquid crystal [3]. -

## Acknowledgments

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# The collective ordering of the magnetic nanoparticles and their influence on the liquid crystal matrix

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An important goal in the research field of liquid crystals (LCs) is the development of novel nanomaterials based on dispersed magnetic nanoparticles (MNPs) to improve their sensitivity to application of magnetic field. Overall, a promising application of these hybrid systems in magnetically driven devices needs a deep insight on the effective coupling between MNPs and LC molecules for optimization of such devices in future technical realization. However, despite of the continuous research of the magnetically-controlled properties of such hybrid composite materials- called ferronematics (FNs), a long-term challenge to address is the problem of colloidal stability of MNPs in LC media. Finally a proper choice of surfactant should aim not only to suppress aggregation but also to minimally affect the properties of LC host. Coating MNPs with (pro)mesogenic ligands has been shown to be a versatile way of their stabilization in LC matrices. We recently report the use of the ligand to disperse cobalt ferrite MNPs in the nematic phase of thermotropic LC 4-pentyl-4'-cyanobiphenyl 5CB [1,2]. Despite their apparently ideal characteristic shape (linear aliphatic structure), a dendrimer coating of MNPs should provide significant higher steric repulsion that leads to a better stabilization in the 5CB LC due to less distortion of the ligand shell. In our study, small angle X-ray scattering, magnetization and capacitance measurements show that dendrimer-functionalized cobalt ferrite MNPs improve magnetic sensitivity of FNs, but have also a tendency to create clusters, and by considering the magneto- nematic coupling, the overall ordering of the LC 5CB is affected due to tilted nematic director field in the vicinity of clusters.

## **Acknowledgments**

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# Varying nanoscale characteristics of a liquid magnet and its effect on the magnetic dynamics

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Stable colloidal suspensions of nanoparticles offer an exciting opportunity to mimic molecular materials and explore their structural and dynamic properties. Recent research has shown that dense dispersions of ferrimagnetic barium hexaferrite (BaHF) nanoplatelets form colloidal nematic phases even in an isotropic solvent such as n-butanol [1-3]. The mechanisms at play depend critically on the interplay of the interactions involved, namely electrostatic and magnetic dipolar interactions as well as steric repulsion. Herein, we provide an overview of our recent findings concerning the experimental study of the magnetization dynamics, which provides invaluable information on the character of the interactions.

We found that even suspensions with low BaHF platelet concentration in 1-butanol a simple Debye-type mechanism cannot describe the complex susceptibility spectrum. Besides the relaxation of single platelets at high frequencies, self-assembly of the particles results in low-frequency contributions, which furthermore depend on the amplitude of the probing AC magnetic field [4]. We additionally found that modifying the particle concentration and therefore varying the magnetic dipolar interactions, or modifying the polar surfactant concentration and therefore varying the electrostatic interactions can either induce or suppress clustering. These effects reflect the nanoscale characteristics of this fluid magnet and therefore its microstructure [5].

## Acknowledgments

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# Ultrasonic emission induced by magnetic fluid hyperthermia

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Energy absorption by Magnetic Nanoparticles (MNPs) under alternating magnetic fields is the source of the heating properties used for magnetic fluid hyperthermia (MFH). Over the last few years it has been shown that, when energy absorption by MNPs occurs in MNPs uploaded cells, biological membranes can suffer physical damage as a consequence of the energy released by the MNP. [1,2] This membrane damage cannot be explained by considering only the effects of temperature. Recently, Carrey et al. [3] have proposed that the generation of ultrasonic waves, in the range of W/cm<sup>2</sup> (eukaryotic cells membrane damage range) due the mechanical oscillation of MNPs under a magnetic field gradient could explain the observed results.

We have developed and validated an experimental setup for the study of mechanical waves generation by MNPs under alternating electromagnetic fields. These experiments were performed at a frequency  $f = 800$  kHz and magnetic flux densities up to 65 mT.

We observed a large increment in the 2nd harmonic value of signal amplitude for the samples containing MNPs that were not present in the nonmagnetic nanoparticles samples control. This constitutes a relevant fingerprint of the ultrasound generation due to magneto-acoustic interaction in the MNPs. Relevant effects observed in uploaded cell with MNPs under MFH could find explanation in the observed effect. [1,2] An efficient targeting of MNPs would also lead to the possibility of performing ultrasound therasnostic by combined acoustic imaging and MFH treatment.

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# Self-assembly and poisoning effect in binary ferrofluids: an experimental study

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Intriguing macroscopic properties of ferrofluids arise from their nanoscale structuring: when magnetic dipolar interparticle interactions are large enough, particles assemble in chains and rings even in the absence of a magnetic field [1]. Binary ferrofluids, i.e. those composed of two types of nanoparticles with different magnetic anisotropies, are particularly appealing because they offer an unprecedented interplay of magnetic dipole interactions [2]. Understanding and controlling interactions between particles could lead to the improvement of the efficiency of known ferrofluids for applications and to the discovery of novel magnetic materials.

In this work, we investigate the relationship between self-assembly and magnetic properties in binary ferrofluids composed of  $\text{CoFe}_2\text{O}_4$  and  $\text{MnFe}_2\text{O}_4$  nanoflowers with various Co:Mn ratios. First, Cryogenic Transmission Electron Microscopy allowed the structural observation of the self-assembly of  $\text{CoFe}_2\text{O}_4$  nanoparticles. The modification of the structuring in binary ferrofluids was then investigated by Scanning Transmission X-ray Microscopy combined with element-selective X-ray Absorption Spectroscopy. Finally, First Order Reversal Curve diagrams were used to probe the magnetic properties of each component in binary ferrofluids by separating the hard and soft magnetic response. We show that  $\text{MnFe}_2\text{O}_4$  nanoparticles become magnetically harder when inserted in the assemblies formed by  $\text{CoFe}_2\text{O}_4$  nanoparticles.

## Acknowledgments

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## Structural and magnetic characterization of superparamagnetic iron oxide nanoparticles for magnetically controlled immune therapy

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Superparamagnetic iron oxide nanoparticles (SPIONs) are promising for biomedical applications such as drug delivery, imaging, and magnetic hyperthermia. In magnetically controlled immune therapy the T cells, which are part of the immune system, are loaded with such SPIONs and accumulate inside a certain region of the body using a magnetic field gradient. The aggregation behavior of SPIONs is crucial for proper utilization and this is determined by their interface properties. Different approaches to interface modification are used to obtain highly cytocompatible and stable particles in biological media, where the most promising ways for water-based solutions are electrostatic and steric stabilization. Thus, detailed knowledge of the inter-particle structural organization and their resulting magnetic properties is of great importance to avoid thromboembolic effects caused by the agglomeration of released particles during future in vivo applications and to optimize the nanoparticle response to the applied magnetic field.

In our work, three different coatings of water-based iron oxide nanoparticles were produced via the co-precipitation method. The morphology of the particles in water was determined by small-angle x-ray scattering (SAXS) and Cryogenic transmission electron microscopy (Cryo-TEM). The TEM results of the citrate- and APTES-coated SPIONs indicate a similar structure with the formation of small particles (6-10 nm) aggregates with the raspberry shape and long-range network agglomerates due to the higher sample concentration, while the dextran-coated NPs show a different structure with a few smaller particles (1-2 nm) and randomly shaped agglomerates with sizes of 30 nm on average. The SAXS results match the Cryo-TEM analysis by getting similar aggregation sizes, but due to the high polydispersity of single particles, no form factor oscillations at high  $q$  were obtained. Magnetometry data points to the classical superparamagnetic behavior of single particles with a small size distribution, but the size distributions of the citrate- and APTES-coated SPIONs obtained by magnetometry seem not to be comparable to those obtained by Cryo-TEM analysis.

Mössbauer spectroscopy in combination with SQUID magnetometry was used to investigate the kinetics of cluster oxidation over time. The advantage of Mössbauer spectroscopy is the ability to obtain information about the oxidation state and magnetic structure of the particles, while magnetometry measurements provide information about the net magnetic properties. For citrate- and APTES-coated SPIONs, the magnetite fraction is reduced to about 25% within a few days and can be extrapolated to a pure maghemite state after a few months. The dextran-coated sample seems to oxidize much faster to maghemite as compared to the other samples, due to the larger surface-to-volume ratio of single particles in the clusters, which increases the rate of oxidation. The decrease in magnetization observable after exposure to air is used as a complementary approach to quantify the rate of oxidation.



## Synthetic Magnetosomes: the development of a nanocarrier for a thermo-active drug respond

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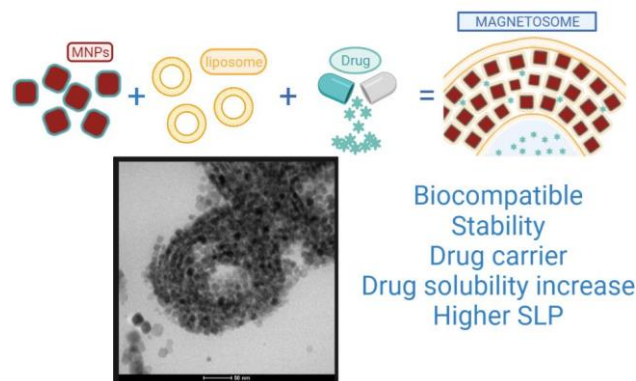
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Novel active release systems based on remote, non-invasive magnetic stimulus are a promise for therapeutic breakthroughs in nanomedicine. Magnetoliposomes [1] and magnetosomes [2] provide some appealing advantages, for instance large cargo capacities, stealth ability and lipidic formulations already approved for clinics. Also, targeted delivery enables increase solubility of actually used drugs and, permit the use of new drugs with nonsuitable pharmacokinetics for clinical use to be implemented. Combining two or more of these capacities would represent a big step forward to increase biologically active molecules at the disease site. We report on a novel nanosystem for thermo-active, magnetically-triggered magnetosomes, together with a recently developed instrumentation to measure the release profiles under magnetic field in real time. We discuss on the challenges of the synthesis and the morphological characterization of the final formulation. From transmission electron microscopy images, we observe curved chains of magnetic nanoparticles (MNPs) covered by lipidic bilayer. In the synthetic magnetosomes arrangement, the MNPs have a higher interaction and provides particular magnetic characteristics compared to the random distribution of MNPs. A mapping distribution of heating values in presence of an alternating magnetic field, reveal a strong dependency with the frequency of both systems, and a higher power absorption for the magnetosomes. In vitro studies show the low toxicity and high internalization of the system.



**Figure 4.** Schematic representation of the structural shape of the synthetic magnetosome.

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# Dynamics of domain formation in a ferromagnetic fluid

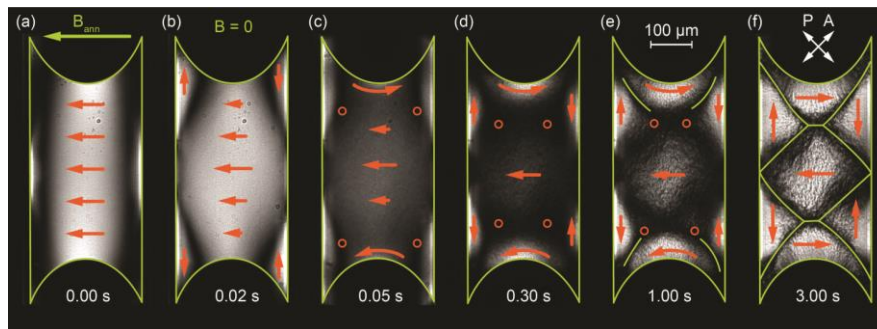
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It has been shown that barium hexaferrite (BaHF) magnetic nanoplatelets exhibit nematic orientational and ferromagnetic ordering when suspended in an isotropic fluid such as n-butanol [1]. While at low volume fractions isotropic suspensions are obtained, at high enough volume fraction anisotropic interactions promote nematic ordering. The critical volume concentration strongly depends on the balance of electrostatic and magnetic interactions [2]. By tuning such interactions via optimization of material parameters such as surfactant concentration or nanoparticle magnetization, we reduced the threshold concentration achieving ferromagnetic ordering at 5.3 vol% [3]. The optimized material allows reproducible and controllable annealing of ferromagnetic domain structures, forming on the time scale of the order of seconds. In this contribution, we report on the formation dynamics of such ferromagnetic domains, with ferrofluids confined in thin capillaries. We analyze the effect of the initial annealing field in the resulting structure, always studied with the compensation of the Earth's magnetic field. In order to estimate the domains' spontaneous magnetization, we explore the effect of an external applied magnetic field on the fundamental fluctuations of the director field inside the domains.



**Fig.1.** Snapshots at different times after removal of annealing magnetic field (green arrow) showing the evolution of magnetization direction (orange arrows). B&W image.

## Acknowledgments

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# Tuning properties of phase-separated magnetic fluid with temperature

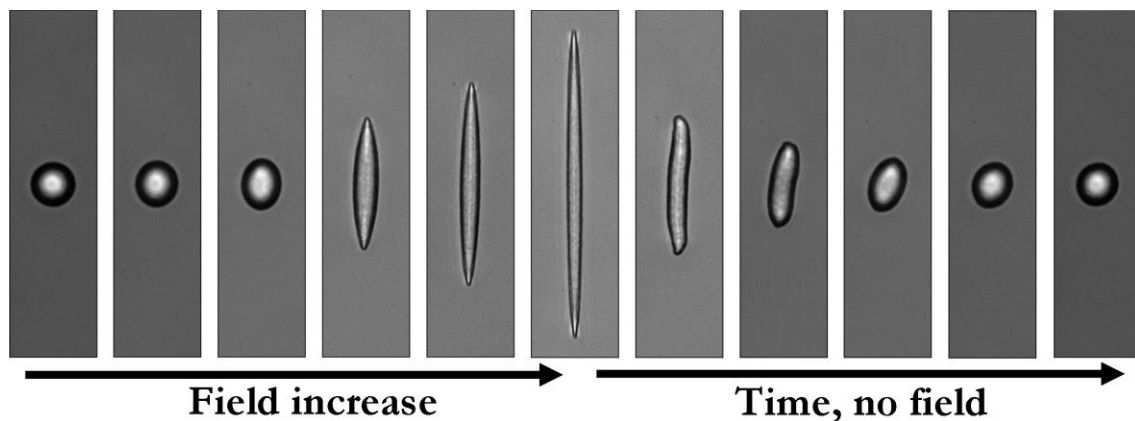
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Phase-separated magnetic fluids provide a very strong magnetic response ( $\mu > 25$ ) in a liquid state material. Even a small field can cause a droplet of the highly concentrated phase present in the less concentrated phase to take a large variety of shapes, including elongated and starfish like [1]. In principle, the droplet behavior can be predicted from the magnetic and viscous properties of both phases, interfacial surface tension and droplet size [1], however, this is a complex system and parameters depend on a variety of factors, often making it difficult to obtain the desired response.

Here we propose to use temperature as the tuning parameter. For that we exploit a microscope with a coil system and a temperature control. The phase-separated magnetic fluid samples are obtained by destabilizing a water based magnetic fluid with a small addition of salt solution. Initially, we use an elongation-relaxation experiment on droplets (see Figure 1) to register shapes and calculate magnetic permeability, surface tension and viscosity [1], while changing the temperature. Long time stability of the system complicates the experiment repeatability, nevertheless our results hint that increasing temperature reduces magnetic properties and viscosity, while surface tension remains constant. We also discuss the applicability of theoretical models used in parameter retrieval. Finally, we use tuning approach on interesting droplet shape transitions, showing the potential of applicability for our findings.



**Figure 1.** Elongation-relaxation experiment for a magnetic droplet

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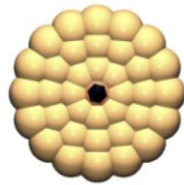
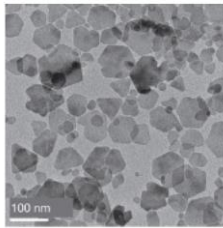
# Impact of Interparticle Interactions on the Dynamic Magnetic Response of Platelets

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For spherical single-domain magnetic particles with permanent magnetic moment, the head-to-tail orientation of the neighboring dipoles is highly advantageous: even if the ratio of magnetic energy to the thermal one is about 3-4, self-assembly is observed. For differently shaped particles, much higher ratios are required for clusters to form. At the same time, for moderately interacting systems the initial static magnetic response of dilute suspensions of shape-anisotropic particles does not differ from that of spheres as the far correlations are nearly the same, and only at close distances the shape manifests itself. When it comes to dynamics, however, it can be expected that shape becomes a key-player due to changes in rotational diffusion.



**Fig. 1.** (left) experimental platelets; (right) simulation platelet

Here, we investigate the dynamic magnetic response of ferrimagnetic Sc-BaHF platelet suspensions with their magnetisation perpendicular to the platelet plane [1,2], using both experiment and computer simulations. We measure the AC susceptibility (ACS) using a custom-made setup with Helmholtz coils generating sinusoidal excitation fields up to 5 mT. In experiment, the platelets are polydisperse (Fig. 1(left)). In simulations, we model a monodisperse system of platelets whose diameter is

equal to the median of the experimental size distribution, the volume fraction of magnetic material is as in experiment and the platelet magnetisation is chosen in such a way that the initial susceptibility in simulation and experiment coincide. Each platelet is built as shown in Fig. 1(right) [3]. We consider two possibilities: either only one dipole is assigned to the center of the platelet, or several of the composing grains are carrying the dipole making the magnetisation distributed. We use Brownian dynamics and Green-Kubo relations to simulate ACS spectra. Along with a qualitative agreement between the simulation and experimental results for the spectra dependence on platelet concentration, such a combined approach allows us to reveal the microscopic reasons behind the spectra shape-changes, allowing in the future a more controlled design of anisotropic particle suspensions.

## Acknowledgements

This work was funded by DFG, projects NA 1668/1-1, LU 800/7-1.

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# Long-Term Measurements of the Magnetization of Suspensions of Isolated Bacterial Magnetosomes

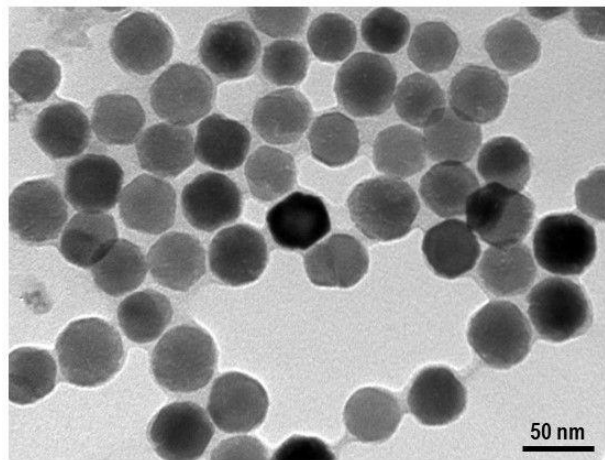
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Magnetosomes (see figure at r.h.s.) are magnetic nanoparticles biosynthesized by magnetotactic bacteria. Due to a genetically strictly controlled biomineralization process, the ensuing magnetosomes have been envisioned as agents for biomedical and clinical applications. In previous work, we examined different stability parameters of magnetosomes isolated from *Magnetospirillum gryphiswaldense* upon storage in suspension (HEPES buffer, 4°C, nitrogen atmosphere) for one year in the absence of antibiotics [1]. The



particle size distribution, the integrity of the surrounding magnetosome membrane, the colloidal stability, and the biocompatibility turned out to be not severely affected by long-term storage. However, when comparing the saturation magnetization of the freshly prepared particle suspension, and that aged by one year, a decay to one third of the initial value was found [1]. To elucidate the aging process, we are measuring since beginning of November 2022 each day four magnetization curves utilizing a vibration sample magnetometer [2], and the study is continuing. The resulting magnetization curves are fitted by means of “graphical granulometry” [3], which allows to monitor the evolution of the magnetic dipole moments, the particle number, and the saturation magnetization.

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# Colloidal Stability of Ferrofluids at 10 T

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In magnetohydrostatic separators, the magnetic field determines whether nonmagnetic materials of a certain density sink into or float on a ferrofluid. A classical application is the separation of diamonds from non-precious minerals, one batch at a time [1]. Dutch engineers have now adapted this approach to separate waste plastics into several density fractions in a single, continuous process, and this technology has been implemented on an industrial scale in Amsterdam and Rotterdam [2]. As physical chemists, we were asked to determine experimentally whether ferrofluids would remain stable at much higher magnetic fields, as may be required in future technology. In theory, it was clear that the answer should be yes, but Nature does not always obey theoretical predictions, as known from weather forecasts, for instance. We therefore were asked for experimental confirmation.

By measuring the sedimentation rate of the magnetic nanoparticles in magnetic fields up to 10 T—via video microscopy inside a Bitter magnet—we could indeed confirm theoretical expectations [3,4]. Ferrofluids that were stable at 0.5 T remained stable at much higher fields. In such a case, detailed analysis of time-dependent concentration profiles showed that sedimentation and diffusion occurred at the rates expected from the magnetic field gradient and the size distribution of the *individual* nanoparticles. Experiments on the length scale of 1 mm and the time scale of a few hours validated a theoretical model that could be used to predict behavior at the much larger length and time scales of the application [4].

## Acknowledgments

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# Experimental investigation of magnetic and self-assembling properties of $\text{CoFe}_2\text{O}_4$ nano-flowers

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The question of particle assembling induced by dipolar interactions was opened by de Gennes and Pincus, who predicted in 1970 the existence of linear chains of nanoparticles in ferrofluids in the absence of an external magnetic field [1]. Despite several theoretical studies that later confirmed this prediction, a conclusive experimental evidence was provided only in 2003 by Cryogenic Transmission Electron Microscopy (cryo-TEM) experiments [2]. When magnetic dipole interactions are large enough, nanoparticles can self-assemble to form linear flexible chains or flux-closure rings, where dipole moments adopt a preferred head-to-tail orientation. At higher concentrations, Monte-Carlo simulations predict a more complex self-assembly scenario [3]. Controlling self-assembly of magnetic nanoparticles in ferrofluids could allow tuning their macroscopic magnetic properties, but a deeper understanding is still needed, especially from the experimental side.

In this work, we investigate experimentally a ferrofluid composed of  $\text{CoFe}_2\text{O}_4$  25nm nanoflowers dispersed in water. Cryo-TEM was first used to study and quantify the various types of self-assembled structures of  $\text{CoFe}_2\text{O}_4$  nanoparticles. Electron holography experiments were then performed to image the magnetic induction lines within different self-assemblies. Finally, First Order Reversal Curve (FORC) diagrams providing the distribution of coercive fields and of interaction fields were measured under Zero Field Cooling and Field Cooling. Our results provide a better understanding of the relationship between the microstructure and magnetic properties of a self-assembled ferrofluid.

## Acknowledgments

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# Topologically-assisted self-assembly driven tilting in nematic liquid crystal hybrids with dendronised nanoparticles

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Self-assembly is one of the crucial mechanisms allowing to design multifunctional materials. Soft hybrid materials contain components of different nature and exhibit competitive interactions which drive self-organisation into structures of a particular function. Here we demonstrate the manipulation of the optical properties of a soft colloidal liquid crystal-hybrid material using a delicate balance between the topologically-assisted colloidal self-assembly of magnetic nanoparticles (MNPs) and the anisotropic molecular interactions. The hybrid material is based on the 5CB nematic liquid crystal with dispersed dendronised cobalt ferrite MNPs with a core size of 4.6 nm [1]. The key feature in the design of these materials is the functionalization of the MNPs, allowing an effective coupling between the magnetic particles and the liquid crystal matrix.

Using magneto-, electrooptical and X-ray studies, we demonstrate that the ferronematic hybrid materials with dendron-functionalized MNPs show a magnetically-induced tilt of the nematic director. We explain this tilt by the formation of mesoscopic, topologically-driven self-assembled chain-like structures of MNPs stabilized through the long-range, director-mediated interactions [2]. The magnetic alignment of these structures is responsible for the reorientation of the liquid crystal director.

## Acknowledgments

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# Optical manipulation of magnetic microparticles

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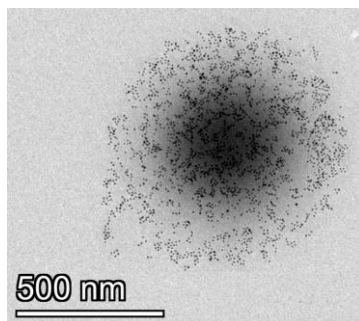
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Optical tweezers allow one to manipulate individual micro- and nanoparticles by means of the momentum transfer of photons that interact with dielectric particles. Such a technique is well suited to, e.g., track their Brownian motion, measure forces applied on them, and probe electromagnetic fields. Trapping absorbing particles is also possible, and in this situation, they act as micro-sources of heat, with interesting applications as hyperthermia [1].

In this work, we explore the Brownian motion of different types of magnetic microparticles, namely, latex-based magnetic microparticles and microgels functionalized with magnetic nanocubes (see Fig. 1). All types of particles absorb laser light and present hot Brownian motion, i.e., a nonequilibrium behavior that takes place when the particle is hotter than the surrounding liquid. Microgels [2] are versatile nanoparticles composed of crosslinked hydrogels which typically exhibit thermo-responsiveness, i.e., they collapse above a given critical temperature. In all cases, we measure the hot Brownian motion of these particles, characterizing the amount of absorbed radiation by the effect on the viscosity of the surrounding fluid. In the case of microgels, we characterize their collapse upon self-heating. We find interesting features, such as heating, convection, and both partial and full collapse of the microgels, which produce bistable dynamics.



**Figure 1.** SEM image of a single microgel decorated with magnetite nanocubes

## Acknowledgments

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# ORAL PRESENTATIONS

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Synthesis



# Magneto-photothermal synergy applied to gold-coated magnetic nanorods

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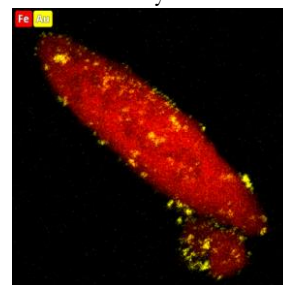
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Magnetic nanoparticles (MNPs) are used in a variety of fields, from industry to health sciences. These nanoparticles can be manipulated by a magnetic field, allowing them to be transported in a specific direction and retained in a specific location. When they are subjected to an alternating magnetic field, the MNPs lose energy in the form of heat, a technique known as magnetic hyperthermia [1]. This technique can be used to kill tumour cells. In addition, MPNs can also be irradiated with a laser of a specific wavelength and intensity, known as photothermia [2]. Both techniques can be used individually or in combination to enhance results, known as dual therapy.



**Fig. 1** Gold-coated magnetite nanorods.

This study presents the synthesis and characterization of magnetic nanorods (NRs) coated with a polymeric triple layer and gold seeds (Fig.1) to improve their biocompatibility and optical properties. The ability of these NRs to produce temperature increases in magnetic hyperthermia, photothermia and dual therapy will be evaluated, and cytotoxicity and drug release assays, of doxorubicin, will be performed [3].

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# Stabilization of magnetic nanoplatelets in nonpolar solvents via dipolar interaction

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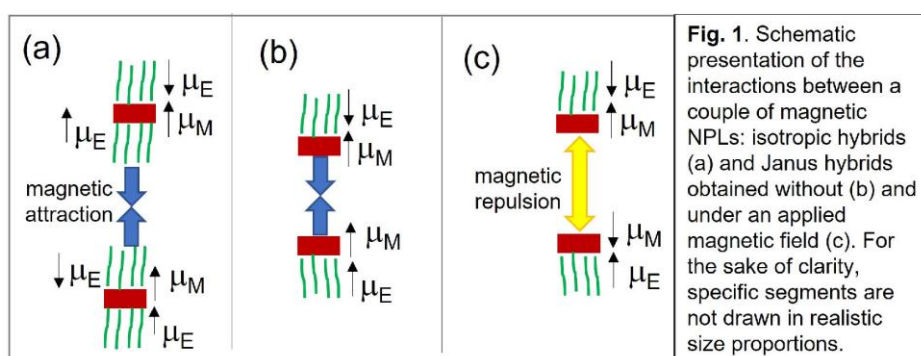
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We will present an atypical mechanism for the stabilization of nonpolar magnetic liquids. Classic nonpolar magnetic liquids, such as ferrofluids, are composed of superparamagnetic nanoparticles functionalized with long nonpolar molecules. The range of repulsive steric forces is determined by the length of a nonpolar molecule and is typically smaller than the range of attractive magnetic-dipole interaction between two permanently-magnetic particles. We propose exploiting dipolar interactions as an alternative to the steric repulsion by long polymer molecules.

We studied the hybridization of barium hexaferrite nanoplatelets (NPLs) with dielectric organic molecules having a large electric dipole moment ( $\mu_E$ ) (Fig. 1). The barium hexaferrite NPLs combine uniaxial magnetocrystalline anisotropy with the shape anisotropy. Consequently, each barium hexaferrite NPL is a nanomagnet with its magnetic moment ( $\mu_M$ ) aligned perpendicularly to the basal plane. By adding the third anisotropy to such a nanomagnet, the attractive magnetic dipolar interaction can be repulsive (Fig. 1c). This was confirmed by hybridizing the NPLs with various phosphonic acids containing 4-(alkylsulfonyl)aniline push-pull system. Janus hybrids obtained at a phase boundary under an applied magnetic field (Fig. 1c) were stable in toluene.



## Acknowledgements

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# Water Transfer of Magnetic Nanoparticles with Different Morphologies using a Ligand Exchange Reaction with a Short-Chained Catechol Derivate

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A proven method for synthesizing magnetic nanoparticles with small size distributions is to synthesize them in high boiling point solvents, resulting in a final product that is a colloidal solution stable in hydrophilic solvents. In contrast, for many applications, the magnetic nanoparticles must be dispersed in aqueous media to function properly. Nanoparticles synthesized in this way are coated with long aliphatic chains that stabilize them in organic solvents through repulsive forces. These ligands can be exchanged by a ligand exchange reaction, giving the nanoparticles new properties, and allowing them to be stabilized in aqueous media if the new ligand is chosen carefully. Of great importance is the retention of the properties introduced in the nanoparticle sample, such as size distribution and shape. In this work, a short-chain catechol derivative (nitroDOPA) in a two-phase system of hexane and water was used to transfer iron oxide ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>) and iron platinum (FePt) nanoparticles into an aqueous solution without changing their properties. The surface of the colloidal nanoparticles was investigated by infrared spectroscopy, X-ray photoelectron spectroscopy, and zeta potential, while the properties of the particles were studied by X-ray diffraction, Mössbauer spectroscopy, and magnetometry.

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## **Magnetic fluorescent nanofluids obtained by a colloidal approach**

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Very recently, magneto-photoluminescent colloidal systems have been intensively investigated considering their versatility by unifying these very compelling characteristics in a single adaptive and responsive smart material. However, the approaches for obtaining such materials often involve encapsulation and/or layering, which hinder the colloidal stability of the final product due to the increased size of the nanocomponents. In this study, we propose a solution to this issue by introducing a novel fluorescent magnetic liquid (FML) synthesized by combining aqueous FFs based on core-shell CoFe<sub>2</sub>O<sub>4</sub>@ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> magnetic nanoparticles (MNPs) with fluorescent nitrogen-rich carbon nanodots (N-CDs) in a colloidal approach [1]. We investigate the hybrid nanofluid in acidic (pH  $\sim$  2.5) and neutral (pH  $\sim$  7.0) conditions, allowing us to probe the effects of different interparticle interactions in the colloidal stability, under the light of the speciation diagrams of each component. Notably, in neutral conditions, (in which an additional citrate coating of the MNPs is required) the FML is visually homogeneous, even under field, as shown in the figure where the samples are shown suspended by a magnet under visible and UV light. The observed macroscopic stability was further confirmed at smaller scales by optical microscopy and small-angle X-ray scattering (SAXS) [2]. In addition, the magnetic properties of the stable FML were checked in a wide range of temperatures and magnetic fields, in which no significant changes were observed compared to unmixed FFs. Nonetheless, the FML's fluorescence emission was considerably modified by the presence of the MNPs, if compared with N-CDs alone. The reduction of the fluorescence emission was mostly attributed to optical absorption and quenching effects. These results demonstrate that in controlled conditions a stable FML can be achieved by mixing FFs and CDs, while largely preserving the individual properties of each nanocomponent. For this reason, the presented hybrid multifunctional fluid successfully combines highly appealing assets into a single product showing a substantial potential for technological applications.

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# ORAL PRESENTATIONS

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*Active systems*



# Deformation behavior of magnetic alginate-methylcellulose hydrogels

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In the field of tissue engineering regarding implants, research is being conducted on cell-laden scaffolds. In order to support cell growth and differentiation processes, the samples are stimulated cyclically. For our approach, we use the cell-friendly, biodegradable hydrogel with magnetite microparticles, as this can be deformed contactless by applying an external magnetic field gradient. Since the deformation behavior is unknown and the material exhibits a time-dependent behavior [1] a cylindrical bending beam as a well-known, simple and good reproducible system was used for characterization. Using an experimental setup with a Maxwell configuration for a  $\mu$ CT, the actual bending curve depending on particle concentration and date can be detected. These are compared with a calculated bending curve based on the Kelvin force. Since this is a novel hybrid material, the unknown material properties such as magnetization and Young's modulus as a function of particle concentration and age were determined for the model by methods adapted for this purpose. The devised model was implemented within the CyMAD bioreactor, which allows cyclic mechanical stimulation [2]. Therefore, also the influence of a stimulation over 14 days with a frequency of 1 Hz for 3 h/d will be presented. On microscopic level particle distribution and structure were analyzed.

## Acknowledgments

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# Ferromagnetic filament shapes reveal their magnetoelastic properties

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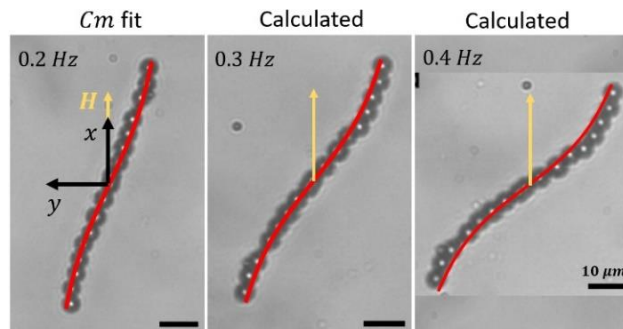
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Microscopic ferromagnetic filaments serve as valuable tools to influence the fluid motion on the micro scale with external magnetic fields; some examples include fluid mixing and self-propulsion [1,2]. The elastic rod model with added magnetic forces has been successfully used to calculate the dynamics of these filaments [1]. To use the model, one first needs to determine the filament's magnetoelastic number  $Cm$  - the ratio of magnetic to elastic forces. Due to the microscopic size, it is hard to measure it directly, and indirect methods are typically used, where the characteristic elastic deformation time  $\tau$  is first determined from the relaxation of a bent filament. This method, however, suffers from the change of the viscous drag coefficient and thus  $\tau$ , depending on the filament's distance to the no-slip surface, which might change depending on how fast the filament is moving.

To determine  $Cm$  more accurately, we devise methods that are independent from the height above the surface. We show that for small  $y/L$ , the filament's shape is described by

$$y = \frac{L\omega\tau}{Cm} \left( \frac{\sinh(x\sqrt{Cm}/L)}{2Cm \sinh(\sqrt{Cm}/2)} - \frac{x^3}{6L^3} + \frac{x}{L} \left( \frac{1}{8} - \frac{1}{Cm} \right) \right), \quad (1)$$

where  $\omega$  is the angular frequency,  $L$  is the filament's length, and  $x \in [-L/2, L/2]$  and  $y$  are defined in figure 1. The ratio  $\omega\tau/Cm$  is determined from the fact that the tip coordinates always describe  $y/x = \omega\tau/(12Cm)$ . Then  $Cm$  is found by the fit of eq. (1). We showcase and validate this method experimentally (figure 1). Another option is to observe the onset of the buckling instability depending on the stationary field intensity. The determination of the filament's physical parameters allows us to use the model to numerically examine more complicated situations such as the flows around micromixers and microswimmers, and quantitatively compare them to experiments.



**Figure 1.** Ferromagnetic filament shapes under 8.2 Oe rotating field. Leftmost image is used to fit  $Cm$ . The red lines are numerical solutions to the model with the determined  $Cm$ .

## Acknowledgments

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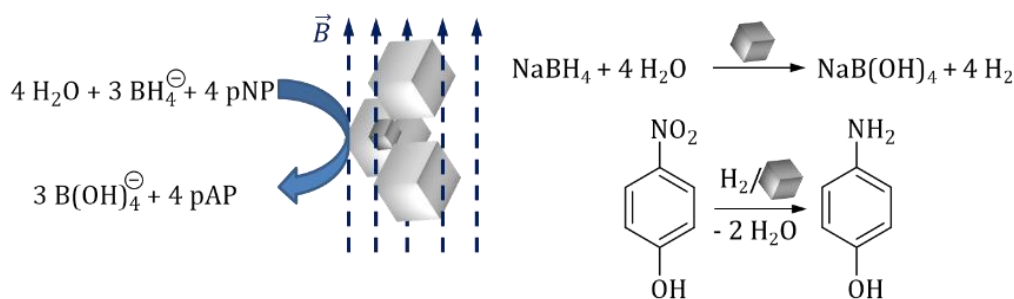
# Single particle tracking of heterofunctional active nanostructures in magnetic fields

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Micro- and nanomotors are small autonomous devices that are capable of performing complex tasks, powered by external forces. Chemical powered nanomotors use the catalytic decomposition of a “fuel” available in their environment. By breaking the symmetry of such structures, an asymmetric flow field in the vicinity of the nanostructure can be generated that leads to propulsion. [1]



**Scheme 1.** Schematic illustration of the catalytic activity of P3.

Investigating the diffusional behaviour of a nanomotor is essential for understanding and thus optimising its design. The approximately 20 nm large system of this work consists of a platinum cube that is occupied by three bigger cobalt ferrite cubes on its corners ( $[\text{CoFe}_2\text{O}_4]_3@\text{Pt} = \text{P3}$ ). While the Pt acts as catalyst in the reduction of *para*-nitrophenol (pNP) in the presence of borohydrides, the  $\text{CoFe}_2\text{O}_4$  cubes are magnetically blocked and allow for a “magnetic riling”. Under optimised conditions, super diffusion and even preferred directionality is observed.

The main tool for the investigation of the diffusional properties of the particle system in water is Single Particle Tracking by dark-field light scattering microscopy (SPT by DF-LSM). With this method, the motion of individual particles is recorded and tracked. Based on these data, important diffusional parameters can be calculated, such as the time-dependent mean squared displacement  $MSD(t)$ , the translational diffusion coefficient  $D$  and, for driven systems, the preferred directionality, the drift velocity  $v$ , the rotational relaxation time  $\tau_R$ , average track lengths and many more.

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# Flexible Magnetic Microcrosses with Programmable Actuation Modes

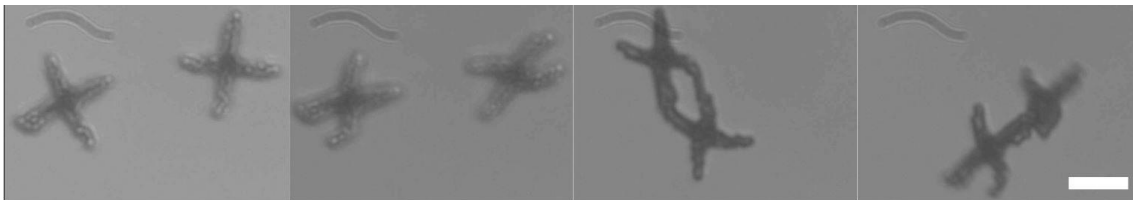
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Man-made devices that facilitate controlled and directed motion at the low Reynolds number limit hold promise for application in a number of areas from in/ex-vivo drug and gene delivery, to unveiling the physics of collective motion at the microscale. <sup>[1,2]</sup>

Such devices come in many forms and can be controlled and actuated with both external and internal energy sources. Of the former, magnetic fields are particularly useful; they are cheap to implement, can be applied in many time-varied forms and are biologically inert. <sup>[2,3]</sup>

Here, we present flexible magnetic microcrosses that are built using a soft lithographical approach and that comprise of a network of connected magnetic particles. In response to different field stimuli, the microcrosses display a range of rotational modes (specifically: smooth rotation, stalling, wagging, leg toggling and break dancing). We build a ‘phase’ diagram of said modes and leverage it to ascertain the magnetic field conditions from which to break the symmetry of the crosses and generate ballistic thrust. Our devices hence have great potential as a starting platform to develop and understand micromachines suitable for targeted functionality on the microscale.



Two flexible magnetic microcrosses approaching, circling and connecting under a circular magnetic field. Scale bar is 10 microns.

## Acknowledgments

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# ORAL PRESENTATIONS

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Theory and Computer simulations



# Magnetophoretic transport of nanoparticles in diluted and concentrated ferrofluids

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Magnetophoresis is a motion of magnetic particles under the action of a nonuniform (gradient) magnetic field. This phenomenon is the basis for many applications of magnetic nanoparticles (MNPs) in biotechnology and medicine (including targeted drug delivery and magnetic cell separation). Quite often, theoretical treatment of magnetophoretic mass-transport in ferrofluids is highly idealized – MNP dispersion is considered as an ideal gas of non-interacting dipoles. Even the non-linear magnetization behavior, one of the key hallmark of superparamagnetism, is sometimes neglected.

In this contribution, we propose a new transport equation for an ensemble of interacting MNPs. It is derived within the LFE theory by Elfimova et al. [1]. The equation accurately takes into account steric, dipolar and hydrodynamic interparticle interactions and does not impose any restrictions on values of the field gradient. To test the new equation, we consider the problem of a MNP redistribution in the vicinity of a current-carrying cylindrical conductor (Fig. (a)). Particle concentration profiles and relaxation times are determined in wide ranges of current values, dipolar coupling constants and net particle volume fractions (Fig. (b)). Theoretical results are critically compared with the results of Langevin dynamics simulations and predictions of other transport equations available in the literature [2].

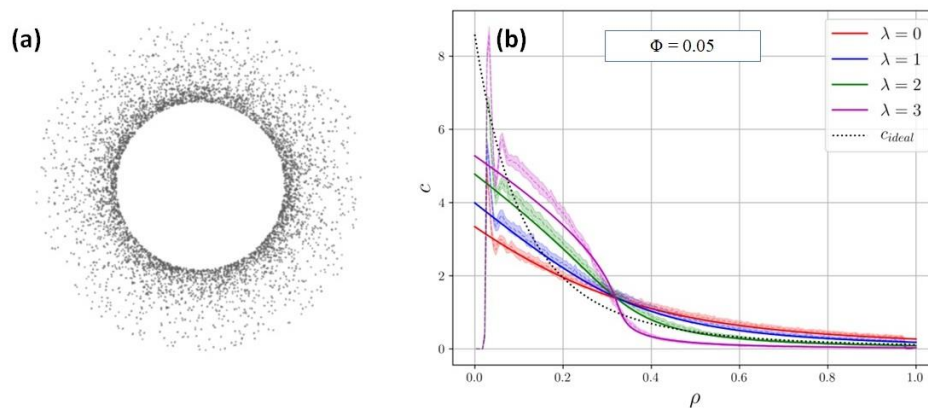


Figure. (a) Simulation snapshot of a MNP ensemble in the vicinity of a current-carrying cylinder (top view); (b) Radial concentration profiles on MNPs at different values of dipolar coupling constant. Solid lines – new theory, dashed lines – simulations, dotted line – ideal gas approximation.

## Acknowledgments

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# Phase behaviour of ferrogranulates in an applied magnetic field

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We show, both in experiment and simulations, that viscoelastic phase separation (VPS), proposed in 2000 by Hajime Tanaka [1] for dynamically asymmetric mixtures, takes place on a millimeter scale in a shaken mixture of steel and glass spheres, called ferrogranulate [2]. In the experiment, a flat vessel filled with a mixture of magnetized steel beads and glass beads is vibrated with high amplitude at 60Hz to preserve a gas phase. Next, it is quenched, and the agglomeration of magnetic spheres is followed optically. In simulations, susceptible steel beads are modelled as dipolar spheres with additional central attraction. The temperature is fixed to mimic the granular temperature caused by shaking after quenching. Simulations were performed with the ESPResSo 4.1.4 simulation package [4]. Complete details of the simulation protocol can be found in [2].

In this contribution, we examine ferrogranulates under the impact of a homogeneous magnetic field oriented in different direction: vertical and horizontal to the monolayer. For certain field amplitudes we observe a three-phase state, namely mobile glass beads, a grid of isolated steel beads and the coarsening network. The experimental results are compared with those of numerical simulations. There is a qualitative agreement between the experimental data and simulation results.

In order to achieve our goal, we calculated different important physical parameters: magnetization (that in perspective can be also accessed in the experiment), dipolar and steric energies, average number of neighbours  $k(t)$  and the efficiency  $E(t)$  of the emerging networks as functions of the simulation time and the values of the external magnetic fields. Next, we construct the phase diagram of ferrogranular in concentration-external magnetic field coordinates.

## Acknowledgments

The research is supported by DFG-FWF Grant I5160.

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# Unveiling the nanoparticle surface effects on AC magnetization: boosting magnetic transduction

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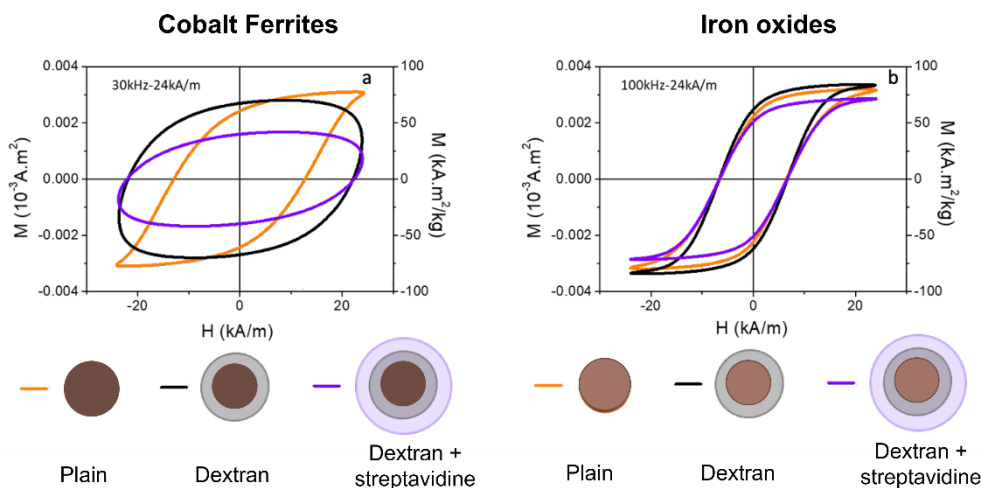
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Recent years has witnessed an increasing interest on the use of magnetic nanoparticles for life science applications. Taking advantage of the transduction capacity of nanoparticles, novel biodetection methods have appeared based on the variation of magnetic signal after biomolecular recognition in liquid media. Such phenomena can be precisely probed by AC magnetometry, which is extremely sensitive to changes on magnetic relaxation process when nanoparticle agglomeration or local viscosity varies under AC magnetic fields in the kHz range.



Here, we report on experimental and computational study on how surface of magnetic nanoparticles influences AC magnetization cycles under alternating magnetic fields ranging from 1 up to 300 kHz and field intensities up to 150 kA/m. Distinct MNPs of similar size and shape but different composition (magnetite or cobalt ferrite) and coating (plain, dextran, PEG or proteins) have been studied. The composition (cobalt ferrite or magnetite) of the magnetic crystal defines magnetic relaxation mechanism (Néel or Brownian, respectively). Figure 1 shows how the MNP surface (i.e., the nanocrystal coating) tightly determines AC hysteresis loops for cobalt ferrite nanocrystals, but not for magnetite counterpart. These results are related to variation of rotational diffusion and numerically simulated in order to provide unequivocal evidences on the high sensitivity of Brownian nanoparticles for transducing surface modifications.

## Acknowledgments

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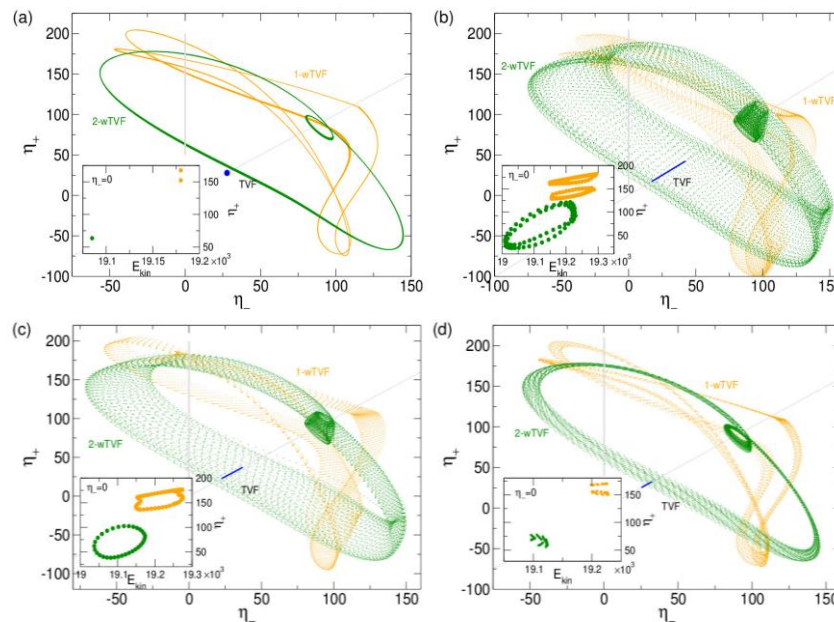
# Ferrofluidic wavy Taylor vortices under alternating magnetic field

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Many natural and industrial flows are subject to time-dependent boundary conditions and temporal modulations (e.g. driving frequency), which significantly modify the dynamics compared with their static counterparts. The present problem addresses ferrofluidic [1] wavy vortex flow in Taylor-Couette geometry [2], with the outer cylinder at rest in a spatially homogeneous magnetic field subject to an alternating modulation. Using a modified Niklas approximation, the effect of frequency modulation on non-linear flow dynamics and appearing resonance phenomena are investigated in the context of either period doubling or inverse period doubling. Flow structures of particular interest in the present work are wavy Taylor vortex flows (wTVFs) [3] (which already have a natural frequency) with main focus on resonance phenomena when the modulation frequency reaches multiples or ratios of the natural, that is characteristic, frequency of the studied flow states.



Phase portrait of 1-wTVF and 2-wTVF under axial magnetic field and different driving frequencies:  
(a)  $\Omega H=0$ , (b)  $\Omega H=15$ , (c)  $\Omega H=30$ , and (d)  $\Omega H=100$ .

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# **Mathematical and Computer Modelling of the Effects of Interactions, Structure Formation, and Polydispersity on the Dynamic Magnetic Susceptibility and Magnetic Relaxation of Ferrofluids**

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Linear response theory relates the decay of equilibrium magnetization fluctuations in a ferrofluid to the frequency-dependent response of the magnetization to a weak ac external magnetic field. The characteristic relaxation times are strongly affected by interactions between the constituent particles. Similarly, the relaxation of an initially magnetized system towards equilibrium in zero field occurs on a range of timescales depending on the structure of the initial state, and the interactions between the particles. The topic of this contribution is the relationship between the time scales for the linear response, and the time scales for relaxation from an initially aligned state.

In this work, ferrofluids are modelled as colloidal suspensions of spherical particles carrying point dipole moments, and undergoing Brownian motion. Recent theoretical and simulation work [1] on the relaxation and linear response of these model ferrofluids is reviewed, and the effects of interactions, structure formation, and polydispersity on the characteristic time scales are outlined. It is shown that:

- (i) in monodisperse ferrofluids, the timescale characterizing the collective response to weak fields increases with increasing interaction strength and/or concentration;
- (ii) in monodisperse ferrofluids, the initial, short-time decay is independent of interaction strength, but the asymptotic relaxation time is the same as that characterizing the collective response to weak fields;
- (iii) in the strong-interaction regime, the formation of self-assembled chains and rings introduces additional timescales that vary by orders of magnitude; and
- (iv) in polydisperse ferrofluids, the instantaneous magnetic relaxation time of each fraction varies in a complex way; the interactions cause the small (fast) particles to relax asymptotically at a rate dictated by the large (slow) particles, which dominate the instantaneous magnetization to which the small particles are coupled.

## **Acknowledgments**

Support by the Ural Mathematical Center, Project No. 075-02-2022-877, is acknowledged.

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# **A fractional step lattice Boltzmann method for complex interfacial behaviors of ferrofluids**

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## **Abstract**

To simulate the complex interfacial behaviors of ferrofluids, a magnetic field coupling fractional step lattice Boltzmann (FSLB) method is proposed. The present FSLB method employs the Chapman-Enskog expansion analysis to reconstruct the convection and diffusion terms of the macroscopic governing equations and uses the equilibrium and non-equilibrium distribution functions to establish the predictor-corrector step. The present FSLB method inherits the excellent performance of kinetic theory from the conventional lattice Boltzmann method and the good numerical stability from the matured fractional-step method. This work successfully performs the first rigorous numerical simulation on the Rosensweig instability, which accurately captures the spikes forming at the surface of a ferrofluid under an applied magnetic field. Moreover, for the first time we numerically reproduce the falling ferrofluid droplet impacted on the solid surface. Intriguingly, our simulation results reveal that the falling velocity of the ferrofluid droplet is slightly accelerated by the elongation, although the direction of the magnetic field is opposite to that of the gravity. All the results for the interfacial behavior and the magnetic interaction highlight the comparative stability, accuracy, and capability of the present magnetic field coupling FSLB method.

## **Acknowledgments**

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# POSTER SESSION 1

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Free Surface Phenomena & Ferrohydrodynamics



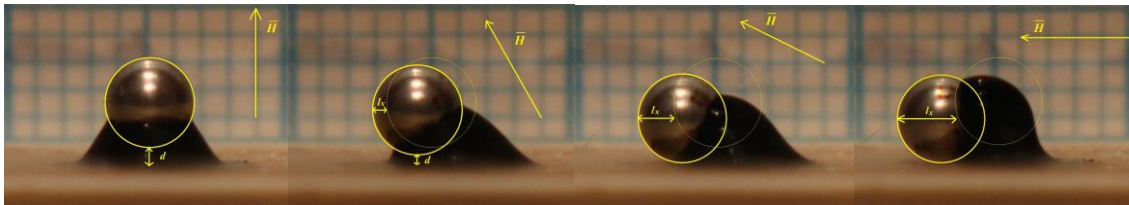
# Control of a magnetic fluid droplet with an immersed magnetizable body by uniform magnetic fields

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The potential of magnetic fluid droplets to be used as miniature reconfigurable soft robots and actuators for a range of biomedical, microfluidic, and lab-on-a-chip applications has been explored by different research groups. The magnetic forces, in combination with the force of surface tension, allow for the magnetic droplet to be manipulated via control of the external magnetic field. Electromagnetic coil systems are usually used to change both position and shape of the droplet either independently or simultaneously. However, such a miniature shapeshifting robot, capable of controlled movement, can also engulf/transport wettable particles or push/manipulate nonwettable particles [1]. Since position and shape control of magnetic fluid droplets by the magnetic field gradient, direction, and magnitude has been well studied, we focus on combined shape control of a droplet and position control of an immersed object (not exclusively wettable or nonwettable) by uniform fields.



**Fig.** Profiles of the droplet with an immersed magnetizable ball in uniform tilted fields.

Thus, realizing that the combination of a uniform magnetic field and magnetic fluid droplet offers wireless and programmable manipulation, we performed experiments and theoretical (both analytical and numerical) studies on how a droplet with an immersed magnetizable body deforms on a horizontal plane under a uniform tilted field (see Figure). A magnetizable ball takes its equilibrium position in the droplet. Spherical shape of the body is chosen for ease of calculating due to a known expression for the magnetic field near the surface of the ball being magnetized in a uniform applied field, but bodies of other shapes were also considered in the experiment. In the noninductive approximation, an analytic expression was obtained for the force exerted by magnetic fluid on the body. We developed a three-dimensional model to predict the deformation of the droplet under uniform magnetic fields of different directions and magnitudes. This research examined the shape control of both immobile and shifting droplets (depending on contact angle), however we focused on the position control of the ball: its levitation height and horizontal displacement. The body position could be controlled by tuning the tilt angle and magnitude of the magnetic field.

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# Effects of couple and surface stresses on ferrofluid flow induced by a rotating magnetic field

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Induced ferrofluid flow by a rotating magnetic field has been an object of scientific interest since it was observed for the first time by Rosensweig *et al.* [1] in 1969. From then on, several theories have been proposed to explain the flow mechanism. Fundamentally, two theories have been established: 1) the magnetic surface tangential stresses [2], and ii) the spin diffusion theory [3]. The latter states that the flow is generated by magnetic body couples acting on the magnetic moment of the nanoparticles, which under the influence of a rotating magnetic field, generate their rotation. The internal angular momentum induced on the nanoparticles is diffused around them and interconverted to linear momentum, by the action of the anti-symmetric stress tensor. On this basis, we studied the experimental ferrofluid flow in a channel reported by Krauss *et al.* [4], which was initially attributed to tangential magnetic stresses at the ferrofluid-air interface. However, experimental velocity profiles in cylindrical recipients (Spin-Up flow geometry) have shown that this flow type can be affected by both surface and volumetric stresses. On the other hand, the phenomenological coefficient of spin viscosity, which quantifies the diffusion of internal angular momentum, has been estimated indirectly from experimental velocity profiles for water based ferrofluid in Spin-Up geometry reported by Torres-Díaz *et al.* [5], recognizing that  $\kappa \sim \frac{R}{\Delta l_{D,exp}}$ , where  $\Delta l_{D,exp}$  is taken as the distance between the surface of the cylinder and the maximum velocity, and  $\kappa$  is a parameter that is inversely proportional to the spin viscosity [6]. We applied a scale analysis to justify each one of the assumptions, to acquire an analytical solution. By implementing Finite Fourier Method, we obtained linear velocity profiles showing both superficial and volumetric stresses or superficial flow only. Velocity profiles showed a reversal flow near the bottom of the channel, which is not observed when diffusion of internal angular momentum is neglected. The dependence of the flow magnitude on the magnetic field strength was 2nd power, while the frequency dependence was approximately linear, owing to the assumption of a linear relationship between magnetization and magnetic field. The reversal flow tended to decrease the magnitude of the flow, in comparison to the surface flow. These results, along with the bulk velocity profiles, can be used to prove (or refute) the theory of spin diffusion as a mechanism generating ferrofluid flow by time-varying magnetic fields.

## Acknowledgments

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# Mathematical aspects in interface analysis of magnetic fluids

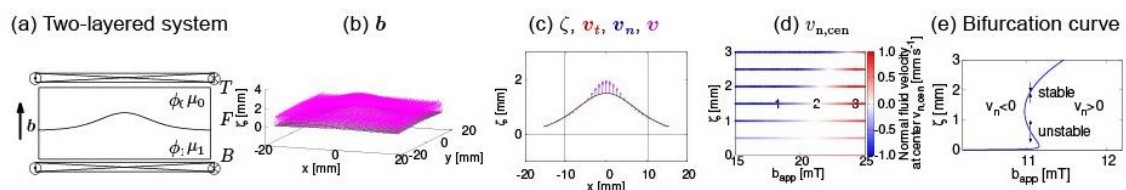
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## Introduction

Numerical platform for stability and dynamic analysis on interface phenomena of magnetic fluids, such as the Rosensweig instability has been constructed [1]. On the interface  $F$  of a two-layered system under homogeneous vertical magnetic field (Fig.(a)), distributions of the magnetic induction (Fig.(b)), stresses such as the magnetic stress difference considering the nonlinear magnetization and the fluid velocity (Fig.(c)) were obtained, based on the Indirect Boundary Element Method (IBEM). Effects of  $S$  (sum of the interface stresses) on the behavior of the interface elevation were investigated. Fig.(d) summarizes the dependence of the  $v_{n,cen}$  (normal fluid velocity at the center of the interface) on  $b_{app}$  (intensity of applied magnetic induction) and  $\zeta_{pro}$  (height of initial interface deformation), to be compared with the bifurcation curve in the Rosensweig instability (Fig.(e)) [2].



## Mathematical modeling

It should be noted that Fig.(d) is the result just after the initial rest state at the infinitesimal time increment  $\Delta t$  where  $v_n \neq 0$  and  $S \neq 0$ , in contrast to the stable bifurcation curve Fig.(e) where  $v_n = 0$  and  $S = 0$  at  $t = \infty$ . Thus, the dynamic analysis from  $t = 0$  till  $t = \infty$  is necessary, considering the changes in the interface profile on the way.

For obtaining  $\phi$  (magnetic potential) and  $b_z$  (normal magnetic induction) for static magnetic field, or  $\varphi$  (fluid velocity potential) and  $v_n$  (normal fluid velocity) for incompressible-irrotational-inviscid fluid, Direct Boundary Element Method (DBEM) has been adopted. In its discretizing process, **multiplicity** of such quantities as  $b_z$  on sharp boundaries is considered. Furthermore, the discretization coefficient in diagonal terms are determined from the sum rule for the discretization coefficients which is derived from the **constant vector field condition**. Remarks while coding and conducting numerical analysis characteristic of magnetic fluids will be discussed as well as the results.

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# Experimental control of viscoelastic phase separation in a ferrogranulate

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“Phase separation is familiar and useful, yet opportunities to manipulate it are surprisingly subtle and complex” was recently emphasized [1].

Therefore, we study the impact of a magnetic field on the phase separation in a shaken granular mixture of glass and magnetized steel beads. Aggregation is occurring in a horizontal vessel after the shaking amplitude is suddenly decreased. Then the magnet-

ized beads form a transient network that coarsens in time into compact clusters, following a viscoelastic phase separation [2,3]. For control, we apply a magnetic field,  $B_z$ , oriented orthogonally to the plane of the network. We measure the average number of neighbours and the efficiency of the emerging network. Both can be fitted by a logistic growth function unveiling that its half-value period increases exponentially with  $B_z$ . Our results demonstrate that via dipole-dipole repulsion the field reduces the mobility of isolated steel beads, thus hindering the growth of the network.

The experimental results are compared with those of numerical simulations.

## Acknowledgments

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# POSTER SESSION 1

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Heat and Mass Transfer





# Temperature evolution equation of a compressible turbulent ferrofluid

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The knowledge of the evolution of temperature is essential to understand the thermal instability and other thermal properties of the ferrofluids. The heat analysis in ferrofluids was initiated by Neuringer and Rosensweig who derived the temperature evolution equation [1]. The aforementioned equation holds good when the fluid is incompressible. B. A. Finlayson [2] derived a temperature evolution equation for a compressible ferrofluid which in the incompressible limit is approximately similar to the one derived in [1]. However, for the study of (i) convective instability far from the conductive regime and (ii) fully developed turbulence in ferrofluids, the aforementioned equations are inadequate and one needs a more general evolution equation of temperature. Addressing all these shortcomings, we have derived a new temperature evolution equation [3] including the compressibility of ferrofluids using basic laws of thermodynamics of moving electromagnetic media, given by

$$\left[ c + \mu_0 \mathbf{H} \cdot \frac{\partial \mathbf{M}}{\partial T} + \frac{P}{\rho} \frac{\partial \rho}{\partial T} \right] \frac{dT}{dt} + \left[ \frac{T}{\rho} \frac{\partial \rho}{\partial T} + \mu_0 \mathbf{H} \cdot \frac{\partial \mathbf{M}}{\partial P} + \frac{P}{\rho} \frac{\partial \rho}{\partial P} \right] \frac{dP}{dT} + \left[ \mu_0 T \frac{\partial \mathbf{M}}{\partial T} + \mu_0 \mathbf{H} \cdot \frac{\partial \mathbf{M}}{\partial \mathbf{H}} + \frac{P}{\rho} \frac{\partial \rho}{\partial \mathbf{H}} \right] \cdot \frac{d\mathbf{H}}{dt} \\ = - \left( \rho \frac{v^2}{2} + \rho I \frac{\omega^2}{2} + P + E_U \right) (\nabla \cdot \mathbf{v}) - \mathbf{v} \cdot \nabla P + \mu_0 \mathbf{v} \cdot (\mathbf{M} \cdot \nabla) \mathbf{H} + \mu_0 \boldsymbol{\omega} \cdot (\mathbf{M} \times \mathbf{H}) - \nabla \cdot \mathbf{q} - \bar{\pi} : \bar{\Lambda} + \mathbf{v} \cdot \mathbf{f}_v + \mu \nabla^2 \left( \frac{v^2}{2} \right) \\ + \frac{\mu}{3} \nabla \cdot [\mathbf{v} (\nabla \cdot \mathbf{v})] - \frac{\mu}{3} (\nabla \cdot \mathbf{v})^2 - \zeta \mathbf{v} \cdot \nabla \times (\boldsymbol{\Omega} - 2 \boldsymbol{\omega}) + \eta \nabla^2 \left( \frac{\omega^2}{2} \right) + \frac{\eta}{3} \nabla \cdot [\boldsymbol{\omega} (\nabla \cdot \boldsymbol{\omega})] - \frac{\eta}{3} (\nabla \cdot \boldsymbol{\omega})^2 + 2 \zeta \boldsymbol{\omega} \cdot (\boldsymbol{\Omega} - 2 \boldsymbol{\omega})$$

where  $c$ ,  $v$ ,  $H$ ,  $M$ ,  $T$ ,  $\omega$ ,  $\mu$ ,  $\zeta$ ,  $\eta$ ,  $I$ ,  $\bar{\pi}$ ,  $\bar{\Lambda}$ ,  $f_v$ , is the specific heat, fluid velocity, external magnetic field, magnetization, temperature, particle spin, dynamic viscosity, vortex viscosity, spin viscosity, average moment of inertia per unit mass, off-diagonal part of the stress tensor, symmetric velocity gradient tensor and external force density. The derived form correctly reproduces the previously obtained forms under appropriate limits. The new equation is extremely useful to study the effect of velocity, particle spin and magnetic field on the evolution of temperature. One can accomplish a detailed and systematic study of thermal convection in ferrofluids *e.g.* Rayleigh-Benard convection and thermal instabilities in a fully developed turbulent ferrofluid flow.

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# Thermal flow analysis of temperature-sensitive magnetic fluid around multiple heated bodies

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A temperature-sensitive magnetic fluid is a magnetic fluid whose magnetization changes significantly close to ambient temperature. Resler and Rosensweig proposed an energy conversion principle that utilizes the properties of this fluid [1,2], and have used a system that self-drives when a temperature-sensitive magnetic fluid is given an appropriate magnetic field gradient and heat. Recently, water-based temperature-sensitive magnetic fluids have also been developed, and researches are being actively carried out assuming their use as cooling devices [3,4]. When using this system for heat transfer, it is necessary to efficiently inject heat into the fluid and generate an appropriate self-drive to transport heat. In this study, assuming that a heat sink is used for heat injection, the heat flow that occurs when multiple heated bodies are arranged in the temperature-sensitive magnetic fluid as shown in Fig. 1. The thermal flow around nine heated bodies was calculated using a hybrid simulation method based on the lattice Boltzmann method, the finite difference method, and the immersed boundary method. Nine prisms or nine cylinders were assumed as the heated bodies. We investigated the local Nusselt numbers on the front, back, and both sides of each body, and the heat flow in case of the prisms and the heat flow in case of cylinders was compared. From the simulation results, it is shown that the heat transfer performance is better from the downstream bodies than that from the upstream bodies. The velocity of the wake is faster in the case of the cylinders than in the case of prisms.

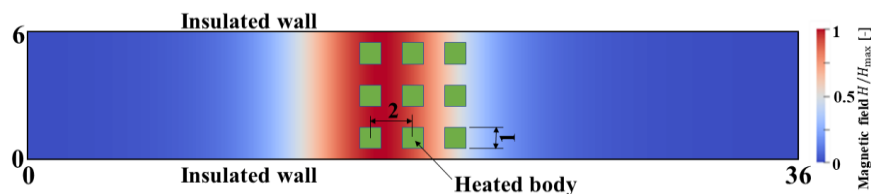


Fig. 1 Analytical model. The representative size is the length of one side of a square.

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# POSTER SESSION 1

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Life and Science Applications



# Maghemite/PLGA (core/shell) nanostructures with potential application in combined chemotherapy and hyperthermia

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## Introduction

Failure of cancer therapy is typically associated to poor accumulation of chemotherapeutics inside malignant cells, and to multidrug resistances. To beat the challenge, combined therapies based on biocompatible nanoparticles (NPs) are under development. In this work, it is described the engineering of a magnetopolymeric nanostructure made of magnetic cores of maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) NPs and a shell of poly(D,L-lactide-*co*-glycolide) (PLGA).

## Methods

Formulation of the core/shell NPs was done by emulsion solvent evaporation technique [1]. Reproducible production of this nanostructure was demonstrated by comparing some relevant characterizations. Short-term colloidal stability was tested at 4 °C. Magnetic responsiveness was characterized *in vitro* by defining the first magnetization curve, and qualitatively by optical microscopy. UV-Vis spectrophotometry and electrophoresis were used to investigate Cisplatin (CDDP) loading. Finally, the *in vitro* heating behavior of the colloid was characterized under exposure to a high frequency alternating electromagnetic field, while the hyperthermia properties were studied on T-84 colonic adenocarcinoma cells.

## Results

The nanocomposites were in the colloidal range (size  $\approx$  270 nm), and the physicochemical characterization confirmed the PLGA shell onto the magnetic nuclei and the adequate magnetic field-responsive behavior. CDDP entrapment efficiency and loading values were  $\approx$  80% and  $\approx$  15%, respectively. Electrophoresis proved CDDP absorption into the NPs. The magnetofluid showed heating capabilities in the electromagnetic gradient, while *in vitro* tests defined a clear decrease in the relative cell viability (up to  $\approx$  43%).

## Conclusions

These  $\gamma\text{-Fe}_2\text{O}_3$ /PLGA nanocomposites hold promising properties for combined antitumor magnetic hyperthermia and magnetically driven drug delivery to malignancies.

## Acknowledgements

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## **Strain promoted azide alkyne click chemistry, an efficient surface functionalization strategy for microRNAs magnetic separation**

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Magnetic nanoparticles (MNPs), used in biological and biomedical assays, like magnetic particle spectroscopy-based applications [1], are made of a superparamagnetic iron oxide core capped with an organic or inorganic layer, to prevent aggregation and to improve their physicochemical stability. Precise surface bio-functionalization is also mandatory to allow highly selective chemical interactions with the biological target to quantify.

In this work,  $\gamma\text{-Fe}_2\text{O}_3@\text{SiO}_2$  core-shell nanoparticles [2] were used to anchor single strand nucleic acid (ssDNA) using two surface functionalization strategies. A comparison of two grafting protocols (figure 1), one based on maleimide chemistry and the other on strain promoted azide alkyne click chemistry (SPAAC) reveals that the SPAAC strategy allows for a higher grafting yield and a more accurate control of the amount of the grafted ssDNA.

Optimized SPAAC grafting protocol enables the grating of six different ssDNA, complementary of miRNA sequences specific of liver (miR 122), skeletal (miR 133b, 206) and/or cardiac (miR 208a, 133a, 1) muscles, as they are promising biomarkers.

Magnetic separation of the complementary miRNA sequences in model buffer solution results in the rapid capture of miRNAs, corresponding to 50-60% of ssDNA's hybridization. Furthermore, capture experiments carried out in complex biological media (fetal bovine serum or rat plasma) reveal only a slight decrease in the amount of miRNA extracted. Finally mismatch experiments using miR 133a and 133b sequences, which differ only by one nucleic acid, indicate a fairly good selectivity.

Dehybridization of captured miRNAs is now being studied in a lab-on-a-chip format using mild magnetic hyperthermia conditions [3] to quantify miRNAs on the surface of microelectrodes, as part of the DIMELEC and e-miRGency projects, funded by the French National Research Agency, and the Labex NanoSaclay, respectively.

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# In vitro evaluation of magnetic fluid hyperthermia therapy on breast cancer cells using monodispered $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoclusters

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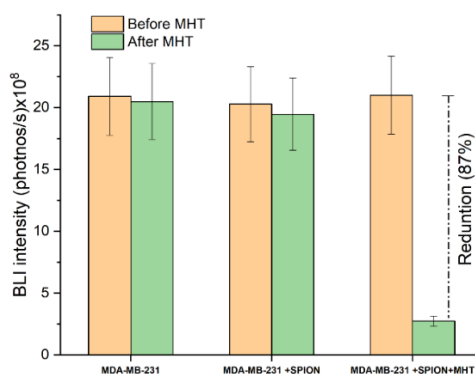
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Magnetic fluid hyperthermia (MHT) is coming up as an alternate treatment therapy of cancer of different types due to its potential low side effects and relatively less painless treatment option. However, the implementation of standalone therapy is still challenges as it is in research phase and needs to optimize the effectiveness to killing 100% cancerous tissues, number of therapy sessions, time duration of the therapy, controlled hyperthermia window temperature, etc. We report here the potential of nanoclusters (nanoflowers) based dispersion and it's in vitro study on breast cancer cells (MDA-MB-231). The nanoclusters were characterized using XRD, TEM, DLS, VSM and MHT before investigating it with the breast cancer cells. Figure 1 shows the effect of magnetic fluid hyperthermia before and after the treatment of induction heating on MDA-MB-231 cells. It is seen that the MHT is capable to kill almost 87% cells within 30 min of treatment on cells in presence of magnetic nanoclusters. This shows a good potential of use of our developed nanoclusters for the treatment of cancer.



**Figure 1.** Effect of Magnetic fluid hyperthermia on MDA-MB-231 cells.

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# Cytotoxicity and uptake analysis of Mn-Zn doped temperature-sensitive ferro-fluid on cervical and bone cancer cells

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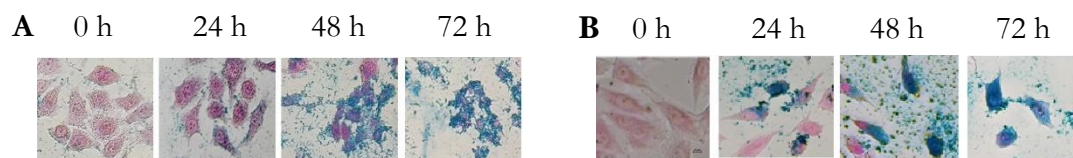
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**Background:** Cancer treatment is the most distressing part of patients' care due to various side effects associated with the different treatment regimes. In this aspect, magnetic fluid hyperthermia (MFH)-based therapeutic strategies are gaining momentum due to their anticipated lesser adverse reactions. However, the precise composition and concentration of MF, time of treatment, and adequate distribution of magnetic nanoparticles (MNPs) in different cancer cells have limited its application which requires thorough investigation. Here, we report the cytotoxicity and uptake of temperature-sensitive lauric acid-coated  $Mn_{0.8}Zn_{0.2}Fe_2O_4$  MNPs in cervical and bone cancer cells HeLa and MG-63 respectively.

**Methods:** The chemical co-precipitation technique was used to synthesize  $Mn_{0.8}Zn_{0.2}Fe_2O_4$  MNPs with  $Mn^{2+} + Zn^{2+} : Fe^{3+}$  in 1:2 ratio coated with lauric acid. The crystalline size of MNPs was obtained using XRD and the magnetic properties of the fluid were determined using a vibrating sample magnetometer. The hyperthermia profile of MF in culture media was determined using 2×2 turns Helmholtz induction heating coils. Cytotoxicity and uptake of MF on cancer cells were determined using MTT assay and Prussian blue staining respectively.

**Results:** The size of MNPs was obtained to be  $11.7 \pm 0.5$  nm. MNPs once dispersed in water showed superparamagnetic behavior. Magnetic fluid at 0.75 mg/mL concentration in cell culture media reached a hyperthermic temperature of 42°C in 80 minutes at 330 A current, 332 kHz frequency and 11.0 kA/m magnetic field. MTT assay revealed  $IC_{50}$  values of 0.767 mg/mL and 0.686 mg/mL on HeLa and MG-63 respectively. Uptake of MNPs keeping MF concentration slightly lower than  $IC_{50}$  values i.e. 0.5 mg/mL revealed partial to complete internalization of MNPs from 24 to 72 hours of incubation in both HeLa and MG-63 cells (Fig. 1).

**Conclusion:** MNPs were successfully internalized by the cancer cells and complete uptake was observed after 72 hours of incubation. However, further analyses are warranted to examine the hyperthermic effect of internalized MF on the cancer cells' death.



**Figure 1.** Internalized MNPs in (A) HeLa and (B) MG-63 cells in blue

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# Optimal composition of zinc-substituted cobalt ferrite nanoparticles for magnetic hyperthermia

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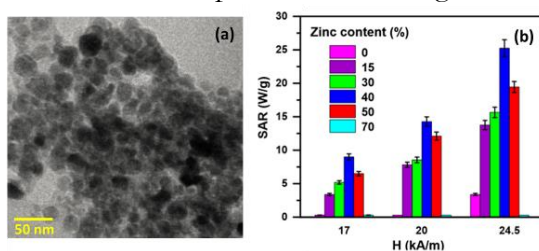
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The unique properties of magnetic nanoparticles (MNPs) have caused them to be one of the focal points of interest in various biomedicine fields. Especially, the remote activation of accumulated MNPs in the tumor sites via an alternating magnetic field can produce the required temperature rise to kill cancer cells, known as magnetic hyperthermia therapy (MHT). The MHT works based on the ability of MNPs to convert the electromagnetic energy of the alternating magnetic field (AMF) into heat; so that they can act as heat-generating nanosources in the cancerous regions [1,2].

Seeking optimal performance in MHT, it is important to have a deep insight into the role of the parameters affecting the heating efficiency of the MNPs, including MNPs physico-chemical properties (size, morphology, chemical composition, etc.) as well as AMF characteristics (strength and frequency). Moreover, finding the interrelation among the effective parameters can give more possibilities to accurately design the high-performance MNPs [3].

In the present work, Zn-substituted cobalt ferrite NPs were synthesized using hydrothermal-assisted co-precipitation method. The MNPs were then coated with a biocompatible polymer to increase biocompatibility and aqueous stability (Figure 1. (a)). The hyperthermia measurements at a fixed frequency (120 kHz) revealed a rising trend of heating efficiency of MNPs by increasing the applied magnetic field strength from 17 to 24.5 kA/m, with the highest efficiency for the optimal chemical composition containing 40% zinc content (Figure 1. (b)).



**Figure 1.** (a) TEM image of MNPs. (b) Magnetic hyperthermia response of MNPs.

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# Dual-responsive magnetic nanorods for biomedical applications

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The development of the multi-functional nanostructures has recently been of particular interest in therapeutic research for various diseases including atherosclerosis, cancer treatment, etc. Indeed, the use of multi-responsive nanostructures that can remotely be activated by different stimuli is a promising strategy to combine the advantages of stand-alone methods and overcome their intrinsic drawbacks.

Thermal treatment using heat-generating magnetic nanostructures which can remotely response to an alternating magnetic field, known as magnetic hyperthermia therapy (MHT), has widely focused on the cancer treatment [1]. Nevertheless, the MHT has recently found applications in thrombosis, inflammation, etc. Mechanical treatment (MT) which is based on the control of the motion of magnetic nanostructures in a rotating magnetic field is another efficient strategy in vascular-related diseases, cancer treatment, etc. [2]. However, combination of the MHT and MT using dual-functional magnetic nanostructures which can well response to both alternating magnetic field and rotating magnetic field can synergically boost their efficiency [3].

In this work, magnetite nanorods coated with a biocompatible polymer have been developed as dual-functional agents for the MHT and MT modalities. The magnetite nanorods showed a high heating efficiency in the MHT and well responded to the rotating magnetic field in the MT. As a main result of the research, the sequential application of the MHT and MT can efficiently be used in biomedical applications including atherosclerosis, cancer treatment, etc.

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## Rotating magnetic fields to enhance the antitumoral action of magnetic nanoparticles

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The development of therapeutic alternatives that allow drug dose reduction and therapy combination, while maintaining (and even improving) treatment efficiency, is a key objective. These efforts are especially necessary in the context of cancer, due to the generation of unwanted secondary effects resulting from the aggressiveness and nonspecificity of the drugs used in chemotherapy. Tumor cells have been shown to be affected by selective mechanical damage caused by magnetic nanoparticles subjected to external magnetic fields. This mechanical damage to the cellular structures is a decisive factor that enhances cell death, which is, therefore, caused by the structural alteration itself and/or by increases in temperature and/or by the production of reactive oxygen species in tumor cells [1].

One way to cause local, targeted damage to cellular structures is by rotating magnetic nanoparticles following upon exposure to rotating magnetic fields. These nanorotors, whose rotation speed can be controlled by these external magnetic fields and which, in addition, can be magnetically directed to the target cell and moved under the action of external fields is a novel approach to the objective of generating localized structural damage in the cells that facilitates the action of active drugs. The present study analyzes the behavior of inorganic magnetic nanoparticles of different morphologies (MNPs) and biomimetic magnetic nanoparticles produced under the mediation of magnetosome proteins from magnetotactic bacteria (BMNPs) when subjected to rotating magnetic fields between 2 and 10 Hertz. The effect of the application of these fields on the viability of tumor cells (HepG2 used as model) treated with all these nanoparticles is also studied in this work.

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## Local antibacterial treatment mediated by rotating magnetic fields

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Antimicrobial therapy is often a research topic of great interest, prompted by the increasing generation of antibiotic resistances that are not paired with the discovery of new therapeutic strategies. Therefore, the design of new strategies to increase the effectiveness of the antibacterial treatments making it possible the reduction of the doses needed to control the infection is a main goal in public health. This is particularly important for Gram negative bacteria, naturally resistant to many antibiotic, due to the existence of the external membrane that prevent the antibiotics to reach their target. However, Gram-negative bacteria have been shown to be affected by selective mechanical damage caused by the rotation of biomimetic MamC-mediated magnetic nanoparticles (BMNPs) following upon their exposure to an alternate magnetic field. This rotation partially disrupted the external membrane, allowing the antibacterial drug to reach the target, causing bacterial death [1].

Therefore, the aim of the study was to study whether or not rotating magnetic fields could also induce mechanical damage on bacterial cell walls that allow the antibacterial drug to reach the target. We have used BMNPs to mediate cell damage following upon exposure to rotating magnetic fields between 2 and 10 Hertz, and the bacteriocin AS-48 as antibacterial peptide, since, thanks to its mechanism of action, the generation of resistances is avoided. We have developed a nanoformulation of BMNPs functionalized with AS-48 and its potential against Gram-positive (*Staphylococcus aureus*, used as positive control) and Gram-negative bacteria (*Escherichia coli*, used as a model Gram-negative bacterium) by itself or combined with exposition to rotating magnetic fields was investigated.

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# Capsules fabricated from liquid marbles and Pickering droplets using magnetic heating

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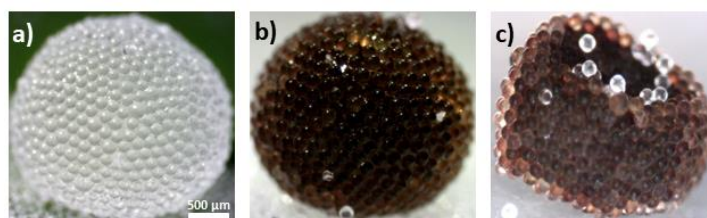
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Colloidal capsules have been investigated in the past few decades due to their potential suitability in medical treatment and diagnostics. When encapsulated, active substances, including drug molecules, can be delivered and released in the site of interest to induce therapeutic effects. On the other hand, capsules can be utilized as contrast agents, e.g., in magnetic resonance imaging or ultrasound imaging.

Different routes can be used to prepare the capsules, for instance, polyelectrolyte complexation, gel trapping, or sintering [1]. In the last case, the high-temperature elevation is required to induce partial fusion of the shell surface and improve its rigidity. Using the alternating magnetic field (AMF) can result in such a temperature increase on a local scale when magnetic nanoparticles act as nano-heaters.

In the presented work, we compared two types of templates used for fabricating capsules. Firstly, particle-stabilized droplets (Pickering droplets) were sintered under AMF covered by iron oxide nanoparticles or immersed in magnetic fluid [2]. Secondly, liquid marbles, i.e., droplets with solid particles accumulated at the air-liquid interface, were filled with magnetic fluid and exposed to magnetic heating (Figure 1). In both cases, the rigid particle shell was obtained, as evidenced by the electric field and mechanical stimulation.



**Figure 1.** a) Liquid marble covered by 140-micrometer polystyrene particles. b) Liquid marble covered by the same particles filled with magnetic fluid. c) Effect of heating under an alternating magnetic field (16.2 kA/m, 355 kHz, 3 min.) on the marble. Scale bar is 500  $\mu\text{m}$ .

## Acknowledgments

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# Magnetic textiles for non-invasive hyperthermia

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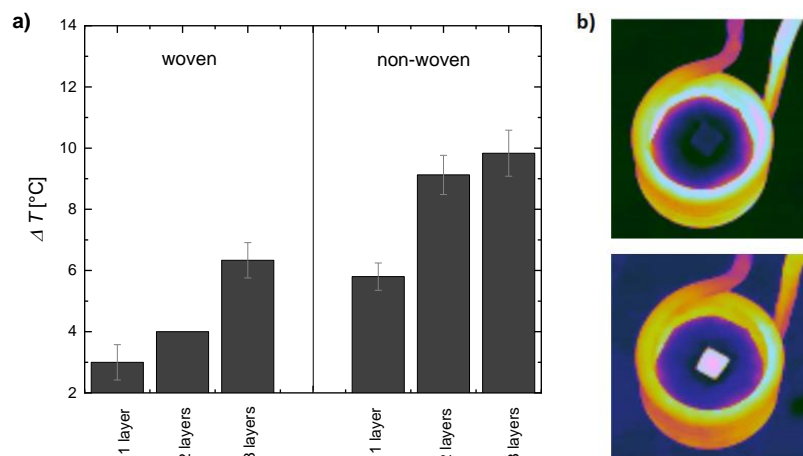
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Magneto-responsive textiles have emerged lately as an important carrier in various applications, including those in biomedical fields such as drug delivery, tissue engineering, and regenerative medicine. To date, most research has been performed on single magnetic fibers and focused mainly on the physical characterization of magnetic textiles. Herein, we designed and characterized simple woven and non-woven textile materials with magnetic properties that can become potential candidates for a smart magnetic platform for hyperthermia treatments.



**Figure 1.** a) Comparison of temperature distribution inside the tissue-mimicking phantom covered with multiple layers of different magnetic textiles used in the study. b) IR image for pure textile and magnetic textile during magnetic hyperthermia.

Experiments were performed on tissue-mimicking materials to test the textiles' heating efficiency in the site of interest. The results suggest that the heat induced by newly designed magneto-responsive textiles led to the temperature increase in tissue-mimicking phantoms depending on several factors, such as the type of basic textile material, the concentration of magnetic nanoparticles deposited on the textile's surface, and the number of layers covering the phantom.

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# Use of nanoparticles functionalized with BSH in BNCT therapy

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Radiotherapy is used in the treatment of cancer in at least 50% of patients, being this method considered par excellence. However, it causes serious complications, especially in patients with recurrent cancer. With the development of new technologies, researchers have developed a number of new approaches aimed to solve this problem. One of them is boron neutron capture therapy (BNCT), based on boron nuclear reactions. This process requires the selective accumulation of <sup>10</sup>B carriers in tumor cells, followed by irradiation of local tissue with a neutron beam, producing the release of large amounts of high-energy particles that kill tumor cells quickly and specifically. To this end, target drugs such as <sup>10</sup>B-borocaptate sodium (BSH) agents have been designed to date. However, it has a moderate selectivity, which encourages the search for new boron release agents that present *in vitro* and/or *in vivo* efficacy in the therapeutic area.

In this context, biomimetic magnetic nanoparticles (BMNP), produced by taking inspiration from nature through the mediation of MamC, a membrane protein present in the magnetosome of magnetotactic bacteria, are a novel system able to bind and carry chemotherapy agents thanks to their properties determined by the MamC protein. The control of MamC during the nucleation and growth of the magnetite crystal allows BMNP to have a size and shape that maximizes their magnetic moment; and, in addition, the presence of MamC results in unique surface characteristics for BMNPs. In fact, MamC provides functional groups and displaces the isoelectric point of the nanoparticle, allowing BMNPs at physiological pH to be able to bind molecules by electrostatic interactions that weaken in an environment at acidic pH such as that found in tumor microenvironments. Given these characteristics, BMNPs have been used as substrate to immobilize BSH as a way to direct the drug to the tumor site, thus reducing the costs and secondary effects associated to the systemic distribution of boron.

## **Acknowledgments**

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# Antibacterial directed chemotherapy using the antimicrobial peptide AS-48 on magnetic nanoparticles combined with magnetic hyperthermia

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Antimicrobial resistance poses a challenge to public health systems worldwide. The urgent need for new and more effective treatments leads researchers to new molecule discovery and the development of more efficient treatments. AS-48 is a circular antimicrobial peptide produced by *Enterococcus faecalis* that targets the bacterial cell membrane in a receptor-independent manner, which is a mechanism of action unexploited in current antibiotic therapies. It has potent activity against Gram-positive bacteria whereas the outer membrane in Gram-negative bacteria hampers AS-48 access to the cell membrane. This causes a reduced susceptibility in these species.

AS-48 has been immobilized on biomimetic magnetic nanoparticles (BMNPs) that resemble those produced by *Magnetococcus marinus*. The binding occurs at physiological pH due to electrostatic interaction between the cationic AS-48 molecule and the negative surface of the BMNPs, and the kinetics fit the Langmuir-Freundlich model. They show a superparamagnetic character after functionalization with AS-48 and a surface negative charge that grants colloidal stability. The nanoassemblies become unstable at acidic pH due to the neutralization of the surface charges of the BMNPs (iep ca. 4.8) and releases AS-48. Thus, the size, stability, saturation kinetics, and magnetic properties of the nanoassemblies have been deeply studied.

A set of three Gram-positive and three Gram-negative pathogenic bacteria has been treated with the AS-48-BMNPs nanoassemblies with and without hyperthermia conditions (45 °C) using an alternating magnetic field (AMF, 22 kA/m 140 kHz). Our data show that neither BMNPs nor 45 °C alone can inhibit bacterial growth. However, when the assemblies AS-48-BMNPs are used they can reach the cell surface and inhibit Gram-positive species and the Gram-negative *Escherichia coli* due to the acidic environment surrounding the cells, but not species that do not decrease the pH (i.e. *Klebsiella pneumoniae* and *Pseudomonas aeruginosa*). Remarkably, when magnetic hyperthermia was applied, the combined triple effect of temperature, AS-48 and mechanical damage caused by BMNP rotation under the AMF, causes a sharp reduction in cell viability within 15 min treatment in all cases, including the initially resistant Gram-negative species.

Our data show that AS-48-BMNPs constitute a potent local treatment of bacterial infections due to the easy directioning using a magnetic field. Moreover, the application of an AMF to locally increase the temperature sensitizes resistant bacteria to AS-48. This new formulation constitutes a novel promising tool against local infections.

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## **Magnetic and structural properties of biogenic magnetic nanoparticles along their production process for use in magnetic hyperthermia: effect of particle arrangement on FORC diagrams**

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Iron-oxide nanoparticles synthesized by magnetotactic bacteria can be used in cancer treatment by means of magnetic hyperthermia. In order to study the structural properties of samples through the successive steps of their production from cultivated magnetotactic bacteria to coated magnetosomes, and their effect on magnetic properties, we performed a combination of (cryo-)Transmission Electron Microscopy observations and magnetic hysteresis as well as First-Order Reversal Curve diagrams at low temperature. The anisotropy of magnetic interactions was investigated by recording field-cooled FORC diagrams with a measuring field either parallel or perpendicular to the field-cooling direction. The results from the various techniques are in very good agreement. We found that magnetosomes in magnetotactic bacteria are arranged in chains and have magnetic properties typical of stable single-domain aligned particles. Extracted magnetosomes form clusters of interacting maghemite particles with some remaining chains, while purified magnetosomes are solely arranged in clusters. Finally, magnetosomes coated with 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) are still organized in clusters but with less magnetostatic interactions than in purified magnetosomes, while magnetosomes coated with citric acid tend to recover a chained structure forming loops. The main features observed on the FORC diagrams are consistent with the various arrangement observed. Lastly, hyperthermia properties were measured for the two coated samples and we found that magnetosomes coated with citric acid display a higher Specific Absorption Rate and therefore hold a better potential for biomedical applications.



## Anti-amyloid activity of proline-, cysteine-, and poly-L-lysine functionalized magnetic nanoparticles

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Protein amyloid aggregation, associated with more than fifty amyloid-related diseases, is associated with structural changes of native protein conformers. Magnetite nanoparticles (MNPs) can affect the formation of amyloid aggregates differently depending on their surface area, size, charge, and concentration. The presented work is aimed to study the *in vitro* effect of MNPs functionalized by proline (Pro-MNPs), cysteine (Cys-MNPs), and poly-L-lysine (PLL-MNPs) on the amyloid aggregation of  $\alpha$ -lactalbumin ( $\alpha$ -LA). These amino acid-functionalized MNPs (aa-MNPs) were analyzed by dynamic light scattering technique, obtaining their hydrodynamic diameter and by laser Doppler velocimetry to characterize their zeta potential and isoelectric point. Thioflavin T fluorescence assay was used to investigate the inhibitory potency of aa-MNPs on  $\alpha$ -LA aggregation. Our results revealed that aa-MNPs inhibit the formation of  $\alpha$ -LA fibrils in a concentration and size-dependent manner. To better understand the mechanism of their anti-amyloid activity, the kinetics of  $\alpha$ -LA fibrillization alone and in the presence of studied aa-MNPs were investigated. All aa-MNPs caused a significant decrease in steady-state fluorescence intensities. Moreover, the presence of Cys-MNPs and Pro-MNPs led to the shortening of the lag phase. Atomic force microscopy visualized the morphology of  $\alpha$ -LA aggregates formed in the presence of aa-MNPs. Shorter fibrils and aggregates with attached aa-MNPs were observed. Moreover, aa-MNPs' cytotoxicity was tested on human embryonic kidney cells. We have found that PLL-MNPs were the most cytotoxic in our study. In conclusion, it was observed that aa-MNPs inhibit the formation of  $\alpha$ -LA amyloid aggregates. The highest inhibitory activity and relatively high viability were shown for the smallest Pro-MNPs. We suggest that Pro-MNPs adsorb  $\alpha$ -LA through hydrophobic patches, blocking intermolecular  $\beta$ -sheet formation. These results indicate the possible application of aa-MNPs for treating amyloid diseases.

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# **Improved Magneto-Microfluidic Separation of Nanoparticles through Formation of the $\beta$ -Cyclodextrin – Curcumin Inclusion Complex**

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Molecular adsorption to the nanoparticle surface may switch the colloidal interactions from repulsive to attractive and promote nanoparticle agglomeration. If the nanoparticles are magnetic, then their agglomerates exhibit a much stronger response to external magnetic fields than individual nanoparticles. Coupling between adsorption, agglomeration, and magnetism allows a synergy between the high specific area of nanoparticles ( $\sim 100$  m<sup>2</sup>/g) and their easy guidance or separation by magnetic fields. This yet poorly explored concept is believed to overcome severe restrictions for several biomedical applications of magnetic nanoparticles related to their poor magnetic remote control. In this presentation, we test this concept using curcumin (CUR) binding (adsorption) to  $\beta$ -cyclodextrin ( $\beta$ CD)-coated iron oxide nanoparticles (IONP). CUR adsorption is governed by host-guest hydrophobic interactions with  $\beta$ CD through the formation of 1:1 and, possibly, 2:1  $\beta$ CD:CUR inclusion complexes on the IONP surface. A 2:1 stoichiometry is supposed to promote IONP primary agglomeration, facilitating the formation of the secondary needle-like agglomerates under external magnetic fields and their magneto-microfluidic separation. The efficiency of these field-induced processes increases with CUR concentration and  $\beta$ CD surface density, while their relatively short timescale (<5 min) is compatible with magnetic drug delivery application.

# Magnetic flower-like nanostructures prepared by different methods

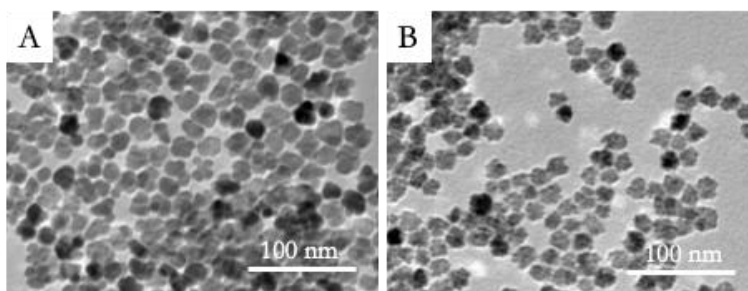
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The colloid aqueous dispersion of superparamagnetic iron oxide nanoparticles (SPIONs) is very popular partly due to their potential theranostic application. Their favorable magnetic properties can be further improved by preparing flower-like structures. There have been some studies in recent years, aiming to prepare magnetite nanoflowers (MNF), however, the preparation conditions are quite different and lack detailed stability experiments. In this study, the MNFs were prepared both in an autoclave and in a round-bottom flask (either with or without continuous mixing) in diethylene glycol (DEG) and *N*-methyl-diethanolamine (NMDA) mixture. The results verified the crucial importance of some preparation conditions, such as the composition of the reaction solvent mixture, reaction time and rate of heating and cooling. Transmission electron microscopic images (TEM) of the nanoparticles revealed that as an effect of mixing, more fluffy structures with an average particle diameter of  $18.3 \pm 2.3$  nm were obtained (Figure 1).



**Figure 1** TEM images of MNF prepared without (A) and with continuous mixing (B)

As a stabilizing agent, based on earlier results [1], poly(acrylic acid-*co*-maleic acid) (PAM) was applied both during and after synthesis. The optimal pH and amount of stabilizing polymer were confirmed by both zeta-potential and dynamic light scattering measurements. During the post-coating method, a minimum of 0.7 mmol/g of polymer proved to be necessary for the stabilization of MNF. To provide information about their potential medical application, beyond the magnetic properties, MRI (determination of the  $T$  relaxation time and the  $r$  relaxivity values), magnetic hyperthermia measurements and hemocompatibility tests were carried out.

## Acknowledgments

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# **The triple combination of chemotherapy, magnetic hyperthermia and photothermia in cancer cells by BMNPs coupled to ChoK $\alpha$ 1 inhibitor.**

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Biomimetic MamC-mediated magnetic nanoparticles (BMNPs) have been established as potent nanocarriers for potential antitumor agents for combined therapy due to their magnetic properties (superparamagnetic character and large magnetic moment per particle under the influence of an external magnetic field), their innovative surface properties determined by MamC protein, their biocompatibility, and their ability to act as photothermia agents under ex-position to Near Infrared (NIR) laser irradiation. On the other hand, lipid metabolism is an important starting point for the design of new anticancer drugs due to the increased biosynthesis of phospholipids such as phosphatidylcholine, among others. So much so that overexpression of a crucial enzyme isoform, choline kinase Choline Kinase  $\alpha$ 1 (ChoK $\alpha$ 1), has been demonstrated in tumour tissue. Among all the inhibitors synthesised for ChoK $\alpha$ 1, a new compound derived from thienopyrimidium bis-biphenyl bis-cationic substituted with a cyclic amine (here named Fa22) shows an extreme ability to inhibit ChoK $\alpha$ 1 activity. However, its use in systemic treatments is limited due to its ability to also inhibit choline uptake and then present low specificity for ChoK $\alpha$ 1. In the present study, we demonstrate that Fa22 coupled to BMNP could offer targeted chemotherapy since allows Fa22 to enter the tumour cell without significantly affecting choline uptake. Furthermore, Fa22-BMNP nanoassembly allows the combination of this targeted chemotherapy with photothermia and magnetic hyperthermia revealing an improvement in terms of decreased drug concentration as well as exposure to physical agents.

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# High throughput analysis of surface-functionalized superparamagnetic particles in dynamic magnetic field landscapes

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In order to meet the growing need for rapid and affordable medical diagnostic tools, Lab-on-a-chip (LOC) devices are investigated as a potential solution by a large and growing scientific community [1]. They can be mass-produced and thus allow, for example, the cheap and fast detection of diseases in developing countries. A promising approach is hereby based on the microfluidic handling of micro- or nanometer-sized magnetic particles (MPs) that are functionalized with capture molecules [1,2]. As an advantage, the MPs are remotely controllable by external magnetic fields. They can then induce specific binding events with analytes in the surrounding liquid, provoking a change in the MPs mobility or equilibrium distance relative to the substrate surface [2].

Here, we demonstrate a novel method harnessing automated optical recognition algorithms to analyze changes in the MPs' motion behavior to liquid-mediated particle-to-substrate interactions, using high-speed camera recordings via an optical microscope.

Using the former, we highlight the distinction of equally sized MPs (2  $\mu\text{m}$  diameter) with two different chemical surface functionalization within a prototypical transport experiment. Here, the MPs were directed within a dynamically transformed magnetic field landscape above a topographically flat magnetic substrate. Our analysis shows possible discrimination between the two MP species purely based on differences in their hydrodynamic drag. This proof-of-principle moves the concept further to life science applications where, e.g., bound viruses only induce a minute change in the MPs surface properties and still allow for a separation of MPs based on their surface functionalization.

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# Interplay between magnetic properties and colloidal stabilization in bio-ferrofluids

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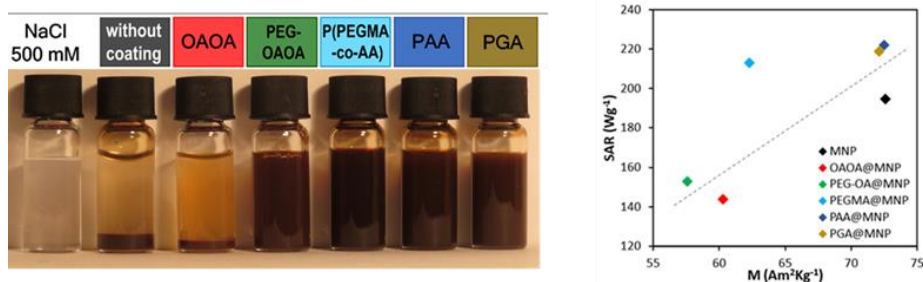
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The present work reports a comparative study on the magnetic behavior of spinel iron oxide nanoparticles (MNPs) coated with different ligands aiming to investigate the interrelationship between the magnetic properties and colloidal stability of the ferrofluids. Spherical spinel iron oxide (magnetite) nanoparticles ( $d_{\text{TEM}} \sim 10$  nm) from the same batch, synthesized by chemical coprecipitation were used as identical cores and various biocompatible ligands, double layer of oleic acid (OAOA), polyethylene glycol with oleic acid (PEG-OA), polyacrylic acid (PAA), polygallic acid (PGA) and a carboxylated PEG copolymer (PEGMA) were chosen to cover the MNPs surface by post coating method. At low temperature, PAA and PGA coatings generate an increase in the saturation magnetization ( $M_s$ ), while the presence of OAOA and PEG-OA shell induces a clear decrease in  $M_s$  after coating, while at the same time excellent colloid stability was observed even at high electrolyte concentrations ( $\sim 500$  mM NaCl).  $\Delta M$  plots showed that the MNPs were slightly interacting systems, which is significantly reduced in the MNP<PEG-OA@MNP<PAA@MNP order. Magnetic hyperthermia efficiencies also increase upon PAA and PGA coating, as shown by their maximum values of specific absorption rate (SAR) of  $220 \text{ Wg}^{-1}$  and  $217 \text{ Wg}^{-1}$ , respectively, as compared to the SAR of naked particles ( $196 \text{ Wg}^{-1}$ ). Nearly linear relationship between the SAR and saturation magnetization values was observed for the coated nanomagnets demonstrating that the post synthetic surface modification of magnetite has a crucial effect on the magnetic behavior in aqueous dispersions.

Figure 1. Salt tolerance (left) and hyperthermic efficiency of the coated nanomagnets (right)



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# Fusogenic liposomes as nanocarriers for the intracellular delivery of magnetic nanoparticles

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Magnetic nanoparticles (MNPs), as any other type of nanoparticles, are internalized by cells through endocytosis, and thus are trapped in intracellular vesicles called endosomes<sup>[1]</sup>. But for a number of bio-applications, such as cellular engineering or magnetic hyperthermia treatments, it can be of great interest to have MNPs able to reach the cell cytoplasm. This would allow to have less dipolar interactions between the MNPs, and hence increase their intracellular heating properties<sup>[2]</sup>. We have recently demonstrated that the functionalization of core-shell magnetic nanoparticles with cationic peptides poly-His promotes their access to the cytosol<sup>[3]</sup>. Here, we propose a novel strategy based on the use of magnetic fusogenic liposomes. Fusogenic liposomes are able to fuse with plasma membrane and as a consequence to deliver their content into the cytosol. We propose to study the fusion of liposomes on a pure electrostatic model already described in the literature<sup>[4]</sup>. Cationic Large Unilamellar Vesicles (LUV, lipid molar ratio DOTAP/DOPE/PEGPE/Topfluor, 1/1/0.1/0.1, 200 nm in diameter) were prepared by extrusion as well as anionic LUV (POPC/POPG, 50:50). Anionic LUV will play the role of acceptor liposomes that mimic the cell membrane. The evolution of the diameter and the zeta potential of the acceptor system is analyzed by DLS, the heat release during the fusion is measured by isothermal titration calorimetry (ITC). This allows the determination of two key parameters that trigger the fusion i.e the best lipid composition and charge ratio (anionic/cationic). Magnetic fusogenic liposomes were then prepared by reverse phase evaporation, the protocol has been adapted from a previous study to avoid the precipitation of anionic MNP in contact with cationic lipids (DOTAP)<sup>[5]</sup>. Their fusion with cell model will be presented.

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# Evaluation of the Application of Multilayer coils in Magnetic Hyperthermia

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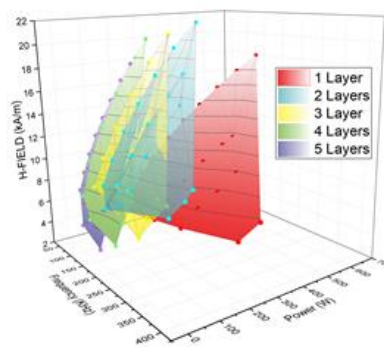
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Magnetic Hyperthermia (MH) is a cancer treatment to destroy tumor cells [1] which effectiveness hinges on the ability to generate H-fields so as to increase the body local temperature between 42-46 °C by means of induction heating and magnetic nanoparticles.

In MH the specific absorption rate (SAR) quantifies the amount of energy absorbed by nanoparticles per unit mass and is directly related with the frequency and the H-field intensity [2]. The latter is determined by the current intensity passing through a solenoid and is directly proportional to the number of coil turns ( $B = \mu_0 INL$ ). However, rising the H- field strength is limited by the power of the system source. Furthermore, increasing the number of turns is not always feasible, since it will produce a decrease in the resonance frequency and electronic problems associated with the oscillator circuit components. In commercial magnetic hyperthermia equipment, single layer solenoids are always used [3].

Here, we improve the generator system by increasing the number of turns/layers. Experimental results and simulations of different multilayer coils reveal an optimal number of layers in terms of the H-field (Fig. 1) and other features of the approach to be considered for MH purposes.



**Figure 1.** Evaluation of the multilayer coils as function of the frequency and power supply

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# Formulation of Methotrexate-loaded magnetite/chitosan nanoparticles

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## Introduction

Conventional systemic chemotherapy involves the administration of large dosages of chemotherapy agents to obtain an acceptable therapeutic effect. However, these high doses can also cause severe side effects at the non-target organs. A very promising solution to this problem is the development of magnetically responsive drug delivery systems. In this work, it is described the formulation of Methotrexate (MTX)-loaded nanoparticles (NPs) consisting of iron oxide nuclei (magnetite, Fe<sub>3</sub>O<sub>4</sub>) embedded into a chitosan (CS) matrix.

## Methods

Preparation of the NPs was done by coacervation [1]. The MTX-loaded Fe<sub>3</sub>O<sub>4</sub>/CS NPs were obtained by dissolving the drug in the aqueous phase before incorporation of Na<sub>2</sub>SO<sub>4</sub>. Reproducible preparation of the NPs was demonstrated by comparing some relevant characterizations. Short-term colloidal stability was tested at room temperature and at 4 °C. Magnetic responsiveness was characterized *in vitro* by defining the hysteresis cycle, and qualitatively by optical microscopy. UV-Vis spectrophotometry and electrophoresis were used to investigate MTX loading. Finally, MTX release was characterized in triplicate by following the dialysis bag method and at the pH of the bloodstream (7.4 ± 0.1), or the acidic environment in the endosomes and lysosomes of tumor cells (pH 5.0 ± 0.1).

## Results

This production procedure led reproducibly to core/shell NPs of ≈ 250 nm in size. Electrokinetic determinations and FTIR analysis helped in qualitatively demonstrating the inclusion of the Fe<sub>3</sub>O<sub>4</sub> particles into the CS matrix. The adequate magnetic responsiveness was confirmed *in vitro*. Formulation conditions were carefully defined to assure an adequate loading of MTX within the CS matrix (EE ≈ 35%). Finally, the pH-responsive MTX release capabilities of the NPs were defined at the normal body temperature.

## Conclusions

These (core/shell) particles may constitute a potential nanotool in cancer chemotherapy.

## Acknowledgements

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# **Doxorubicin-loaded iron oxide nanoparticles for chemo-thermal synergistic therapy of cancer**

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Nanotechnology offers the possibility of developing innovative, more efficient and safe treatments based on nanostructures, emerging a new field of research, nanomedicine. These nanoparticles can overcome cellular and physiological barriers and provide favorable biodistribution, bioavailability and improved pharmacokinetics of desired drugs [1]. They can also target entities in the tumor environment and induce physical therapeutic effects after being stimulated by a remote signal, allowing for site-specific treatment. These treatments can limit unwanted side effects by preventing damage to surrounding healthy cells. One of the most promising treatments is hyperthermia. Hyperthermia therapy is an anticancer clinical practice based on elevation of the tumor temperature, driving malignant cells and tissues up to the cytotoxic level, that is, 43-48 °C [2]. In addition, cell resistance against traditional treatments, such as chemotherapy or radiotherapy, can be reduced. In this work, we report the synthesis of a multimodal therapeutic system based on iron oxide nanoparticles (IONPs) loaded with a chemotherapeutic agent, doxorubicin (DOX). IONPs are widely used in biomedicine and have been approved as contrast agents for magnetic resonance imaging (MRI) [3]. Furthermore, IONPs are excellent candidates for magnetic hyperthermia (MHT). Therefore, we propose a multimodal treatment that combines local chemotherapy with efficient thermal therapy, to obtain a remarkably effective treatment due to the synergistic effects of the therapies. Biocompatibility and internalization capacity of IONPs in cells were examined, as well as the release and localization of the drug before and after thermal therapy. After hyperthermal treatment, this initial co-localization of DOX in lysosomes is lost. We can conclude that DOX-loaded IONPs are excellent agents for chemo-thermal therapy after an adequate functionalization of the IONPs.

## **Acknowledgments**

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# POSTER SESSION 1

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Magneto-Polymer Composites



# In-situ observation of the influence of magnetic field and temperature on the particle microstructure of thermoplastic polyurethane magnetorheological elastomers

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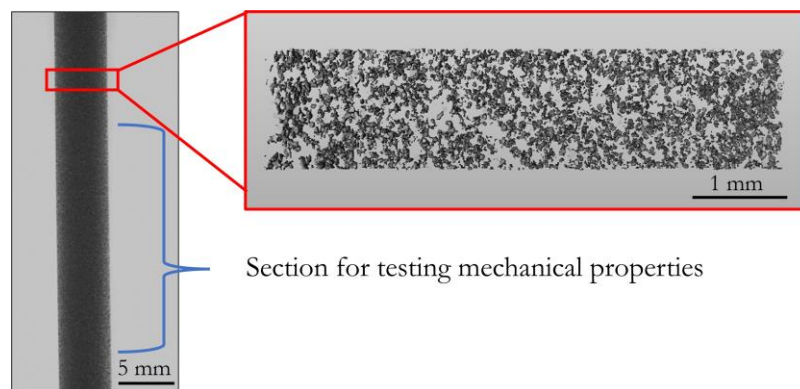
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Magnetorheological elastomers (MREs) are smart composite materials, composed of magnetic particles suspended in an elastomeric matrix. This way the stiffness of the composite can be manipulated by changing the applied magnetic field. In general, MREs with silicone elastomer as matrix material are studied and used due to their inert property and ease of preparation. In recent times thermoplastic elastomer based MREs have gained much importance due to their additional functionalities. Among thermoplastic MREs, polyurethane elastomer based MREs are most widely studied due to their superior mechanical properties, ease of modifying their physical properties and recyclability. Thermoplastic polyurethane MREs (TPU-MREs) can be stimulated by both temperature and magnetic field.

Cylindrical rod-shaped TPU-MRE sample with 40 wt.% of iron particles were synthesized. The microstructural investigation of the samples under the influence of different temperature and magnetic field was performed using X-ray microcomputed tomography. The samples were observed for microstructural changes at 23 °C and 60 °C without and with a magnetic field of 250 mT. The microstructural distribution of particles was investigated using pair correlation function (PCF) and the influence of different stimulating conditions were studied. In addition to this samples from the same batch of production were used for investigating the mechanical properties like Young's and shear modulus under no pre-induced strain conditions. This allows for precise correlation of the influence of stimulating conditions on the observed microstructural changes causing the changes in macroscopic properties of the material.

Financial support by DFG in the project OD18/28-1 within the priority program SPP2100 is gratefully acknowledged.



Radiogram of the TPU-MRE sample (left) and its reconstructed cross-section image (right).

# High-Performance Semi-Interpenetrating Magnetic Hydrogels: Applications as Magnetic Optical Sensors and Magnetic Valves

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During the last years there have been an increasing interest in the design of novel magnetic hydrogels for applications in different technological fields such as artificial muscles, soft machines and actuators, and valves for fluidics systems. The interest in them is due to their unique characteristics like their softness, high water content, and fast response under a magnetic field, even though certain issues must be addressed like their relatively low stretchability and toughness, and their notch-sensitivity. One strategy commonly used to synthesize these hydrogels is interpenetrating and semi-interpenetrating polymer networks, which combines functional properties of distinct polymers, which in previous works have proven to reduce the brittleness of magnetic hydrogels [1]. In our work, we have developed semi-interpenetrating polymer networks based on polyacrylamide and different biopolymers with embedded iron silica coated micro-particles. Mechanically, we studied these materials under compressive, tensile and shear stress, obtaining different moduli as well as the maximum strain which the materials can bear. From these results, we conclude that the presence of the magnetic micro-particles reduces the stiffness of the hydrogels while a high stretchability and compressibility are maintained (up to 220% under tensile stress and 92% under compressive stress). Finally, we applied our novel magnetic hydrogels as intelligent valves in a milli-fluidics system and as a two-phase magnetic optical sensor.

## Acknowledgments

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# Microstructural analysis of a magnetic polymer containing liquid metal

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Recently, numerous investigations have been conducted on the physical properties of mixed polymer and liquid metal composites, demonstrating perspectives of their usage in various types of applications, see e.g. [1]. Furthermore, it has been very recently proposed to combine such type of a composite with magnetic filler, toward liquid metal based magnetorheological elastomer (LMMRE) [2]. Certain macroscopic properties of such composites have been investigated and a number of sensor oriented applications has been proposed [3]. Our preliminary studies have shown some challenges with the reproducibility of systematic results concerning the physical properties of these composites. This issue may be related to the heterogeneity of the size and distribution of the liquid metal droplets in the matrix. Thus, within this study we present results of microstructural investigations of a multicomponent LMMRE composite. Specifically, we use silicone elastomer as an elastic polymer matrix, magnetically hard NdFeB alloy filler microparticles as a magnetically controlled phase, and GaInSn eutectic alloy as an electrically conductive liquid phase. The utilization of a magnetically hard filler expands the functional capabilities of the magnetoactive composites by providing the ability to tune the material properties after crosslinking [4], while active control remains possible. The study is carried out by computed microtomography, which we have previously adapted for magnetic hybrid materials [5]. In addition to visualizing the three-dimensional internal structure of a multicomponent functional magnetically controlled material, we investigate the effect of composite fabrication parameters on its final microstructure. These include the speed and duration of mixing of the components as well as their concentrations. Based on microstructural data, we demonstrate that certain production process criteria must be met in order to produce homogeneous samples.

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# Shrinking behavior of thermo-and magnetic-responsive gels under external magnetic fields

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## Introduction

Thermo-responsive hydrogel composed of *N*-isopropyl acrylamide (NIPA) reversibly shrinks above lower critical solution temperature (LCST),  $\sim 32^{\circ}\text{C}$ . The addition of magnetic nanoparticles (MNPs) into the NIPA gels gives magnetism to the gels; thermo-and magnetic-responsive MNP-NIPA gels are obtained. Although shrinking-ratio rise after MNP addition and position control of MNP-NIPA gels using external magnetic fields (MFs) have been discussed, the effect of MFs on gel-shrinking ratio remains unclear. Hence, the effect of the MF application was investigated using MNP-NIPA gel sheets in this study.

## Experimental Results

NIPA-MNP gel sheets of  $10 \times 10 \times 1 \text{ mm}^3$  were prepared and the shrinking ratio, when the ambient temperature was changed from  $20^{\circ}\text{C}$  to  $40^{\circ}\text{C}$ , was determined by measuring the mass of the gel sheets. The MF was applied by using a neodymium magnet. NIPA-MNP gel sheets at  $40^{\circ}\text{C}$  with MF were shrunk compared to a state at  $40^{\circ}\text{C}$  without MF because MF application generates aggregation force between MNPs (Fig. 1(a),(b)). The shrinking gel was not restored even after MF removal unless the gel was cooled to  $20^{\circ}\text{C}$  since swelling force is not generated unless the gel cooled to below LCST (Fig. 1(b)). We also investigated the repeatability of shrinking-ratio rise by MF application. There was no change in the shrinking behavior of the gels in three cycles (Fig. 1(b)). These results imply the possibility and repeatability of shrinking-ratio control utilizing the strength of MFs.

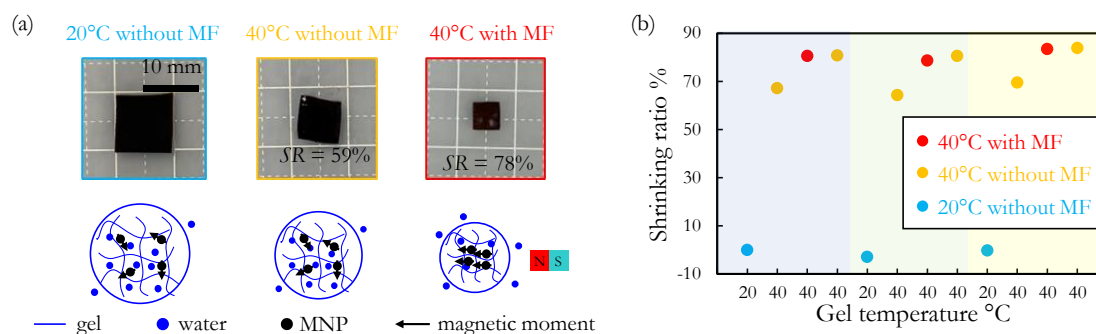


Fig. 1. (a) Photographs, shrinking ratio ( $SR$ ), and schematic illustration of NIPA-MNP gel sheets at  $20^{\circ}\text{C}$  and  $40^{\circ}\text{C}$  with/without MF application, and (b) shrinking ratio of NIPA-MNP gel sheet treated for three cycles ( $20^{\circ}\text{C}$  without MF  $\rightarrow$   $40^{\circ}\text{C}$  without MF  $\rightarrow$   $40^{\circ}\text{C}$  with MF  $\rightarrow$   $40^{\circ}\text{C}$  without MF  $\rightarrow$   $20^{\circ}\text{C}$  without MF)

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# Organic-inorganic microparticles produced by heat dissipation of magnetic nanoparticles

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## Introduction

Heat dissipation of magnetic nanoparticles under alternating magnetic fields has been developed in an area of medical treatment such as drug delivery and magnetic hyperthermia [1,2]. The present study demonstrates another application of the heat dissipation: the use of organic-inorganic hybrid microparticle manufacturing. We expect the microparticles to be applicable for precursors of magnetic activated carbons and organic porous particles.

## Experimental

Microparticles composed of thermoset polymer polydimethylsiloxane (PDMS) and magnetic iron-oxide nanoparticles (IONPs) were manufactured by utilizing the heat dissipation of the IONPs, as shown in Fig. 1(a). Uncured PDMS and IONPs were mixed, and then the mixture was exposed to an alternating magnetic field. The PDMS surrounding IONP agglomerates was cured by heat dissipation resulting in the formation of microscale composite particles.

## Results

Fig. 1(b) shows SEM and STEM images, and STEM-EDX elemental maps of PDMS-IONP composites formed in 1 wt% IONP mixture exposed to a magnetic field of 2 MHz and 50 Oe for 1 h. Spherical composite particles of about 0.5-1  $\mu\text{m}$  in diameter were formed in the conditions. We discuss the effect of the magnetic field conditions on the structure of obtained particles in the presentation.

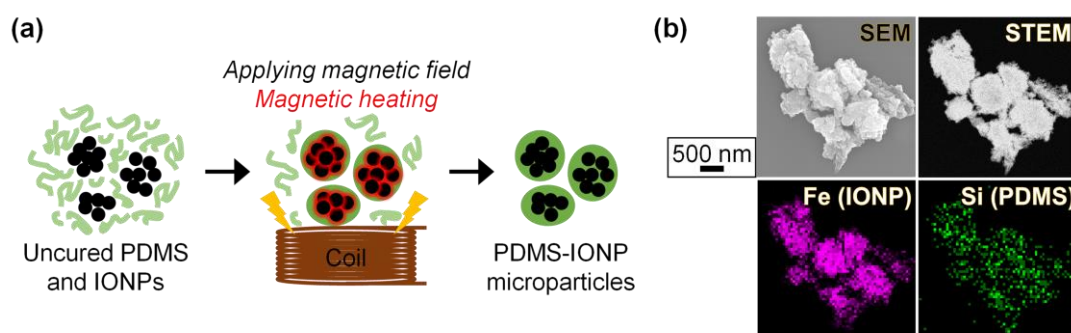


Fig. 1 (a) Manufacturing procedure of PDMS-IONP microparticles, and (b) morphology (SEM and STEM images) and STEM-EDX elemental maps of microparticles.

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# Accessing nanoscopic viscoelastic properties of polymeric microgels using magnetic nanoprob

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Stimuli-responsive polymeric microgels ( $< 1 \mu\text{m}$ ) have wide spread applications as sensors, actuators or drug delivery vehicles<sup>1</sup> owing to their fast response to external stimuli. Measuring the macroscopic properties of hybrid (crosslinked) polymeric gel is well established, but extrapolating macroscopic understanding does not always explain physical/mechanical properties at the nanoscale. The nanoscopic properties of complex polymer based systems are known to be probe size dependent and give rise to different viscoelastic properties based on the dimension of probes compared to the correlation lengths of the polymer network<sup>2</sup>. In this regard, magnetic nanoparticles (MNP) can act as an ideal probes to investigate the nanoscopic viscoelastic properties of microgels. Thermally blocked MNPs undergo Brownian relaxation when excited with a high frequency alternating magnetic field ( $\sim 100$  kHz). Accordingly, AC susceptometry-based measurements can unveil magnetic relaxation phenomena at various length scales and are capable of providing local viscoelastic properties.

PNIPAM microgels, synthesized with varying crosslinking density, are used as a model system of investigation. The microgels are synthesized in the precipitation-polymerization method using 2,2'-azobis(2-methylpropionamide) dihydrochloride as an initiator for obtaining positively charged microgels (size  $\sim 221$  nm at  $50^\circ\text{C}$ ). Cobalt ferrite nanoparticles ( $\sim 16$  nm) with negative surface charge are incorporated in the microgel by charge assisted diffusion to obtain magnetic microgels (shown in Fig. 1). AC susceptometry spectra of MNPs in water are distinctly different from the MNP-embedded MGs (Fig.1 c & d). The shift of the peak of  $\chi''$  to a lower frequency is indicative of slower Brownian relaxation of MMGs. The degree of crosslinking of the microgel is varied using different comonomer ratios (BIS: NIPAM), which in turn influences the coherent length and thus changes the nanoscopic viscoelastic properties. This is investigated using AC susceptometry and nanoindentation methods, and will be subsequently probed with simulations.

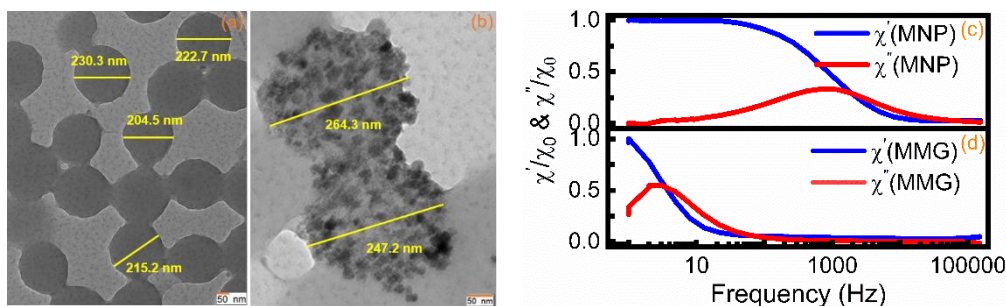


Fig. 1 TEM micrograph of dried microgels (a) and magnetic microgels (b). AC susceptibility spectra of MNPs (c) & MMGs (d) in water.

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# Ferrite-based Magnetic Nanoparticles in a Smart Polymer Matrix

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For hyperthermia applications, reproducible synthesis routes of magnetic nanoparticles (MNP) with control and adjustment of the structure, size, shape and magnetic properties are the key aspects. To minimize the adverse side effects on healthy cells, a large amount of heat generated by a small quantity of nanoparticles must be delivered to the tumor cells only. Therefore, particles with large values of saturation magnetization and a high resolution for magnetic imaging are required leading to a strong and efficient response to the external magnetic field. Among the ferrites, magnetite ( $\text{Fe}_3\text{O}_4$ ) has the largest magnetic moment, but it grows into an isotropic form for thermodynamic reasons and has a correspondingly small magnetic anisotropy constant. Furthermore, cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) has turned out to be an interesting material as spherical cobalt ferrite shows a higher magnetocrystalline anisotropy than iron oxide.<sup>1</sup> As the reduction of the  $\text{Co}^{2+}$  ion concentration in cobalt ferrite particles leads to an increase in average crystallite size, coercivity, and saturation magnetization,<sup>1</sup> our work is focused on the synthesis of non-stoichiometric cobalt ferrite nanoparticles. In a two-step reaction, akaganeite nanorods (an antiferromagnetic iron oxide hydroxide) were prepared first followed by an aqueous hydrothermal reaction without toxic surfactants or solvents and variation of the metal salt concentration and composition of  $\text{Co}^{2+}/\text{Fe}^{3+}/\text{Fe}^{2+}$ . Examination of the magnetic characteristics of the nanoparticles and hyperthermia measurements will be systematically conducted to consolidate the heating efficiency of the as-synthesized MNP. These particles should already be dominated by the Brownian relaxation mechanism in the high single-digit nanometer range from about 7 nm compared to magnetite nanoparticles, which are dominated by the Néelian relaxation mechanism up to a critical particle diameter above 14 nm.<sup>2</sup> An extensive field in material science is developed by embedding these “hard” magnetic nanostructures within an organic “soft” matter. In our working group, we focus on the combination of magnetic cobalt ferrite and magnetite with a crosslinked gel matrix consisting of a *graft*-copolymer to afford a thermo-responsive hydrogel and, exemplarily, application in the field of polymer therapeutics.<sup>3</sup>

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# Exploring the particle–matrix coupling in soft magnetic polymer hybrid materials

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AC-susceptometry is a powerful experimental tool to study the local properties of magnetic-polymer hybrid materials. In particular, the local viscoelastic properties of the polymer matrix can be studied, and the coupling between magnetic nanoparticles and the polymer elucidated.

In our contribution, we show corresponding simulations on magnetic nanoparticles in a polymer solution. We combine coarse-grained molecular dynamics for the magnetic nanoparticles and polymers with lattice-Boltzmann hydrodynamics.

In such a simulation, it is possible to switch on specific interactions, such as magnetic, steric, van-der-Wals, or hydrodynamic, individually. Hence, their relative importance can be studied.

In particular, we demonstrate that hydrodynamic interactions on their own can reproduce the experimentally observed trends in AC-susceptibility spectra for spherical magnetic nanoparticles in a polymer solution.

Non-spherical particles are a promising candidate for strengthening the particle-polymer coupling, as their rotation would force surrounding polymers to move due to steric interactions. However, we show that even for ellipsoidal particles, hydrodynamic coupling between the nanoparticles and the polymers dominates.

In an outlook, we take a first look at magnetic nanoparticles in polymer networks, examining e.g., the influence of the mesh width on the mobility of magnetic nanoparticles.

## **Acknowledgments**

We acknowledge support through the Cluster of Excellence EXC 2075 SimTech, funded by the German Science Foundation, grant no. 390740016.

# Effect of particle-dispersion process on magnetic-chain-templating unidirectional pore formation

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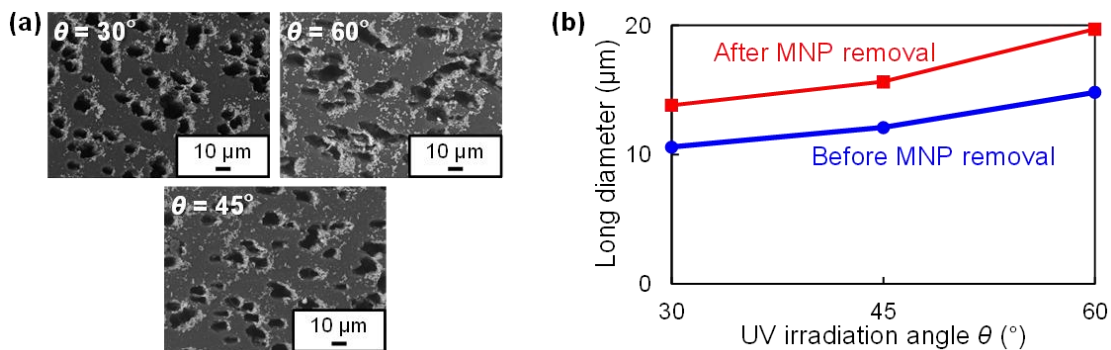
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## Introduction

Unidirectional porous resin has high fluid permeability and low thermal conductivity, thus, can apply to thin capillary-driven heat transfer devices. We have reported a manufacturing method of unidirectional porous UV curable resin using magnetic-nanoparticle (MNP) chain templates [1]. The obtained porous samples had cylindrical pores with an ellipsoidal cross-section. Although the pore ellipticity varied with the UV irradiation angle, the long diameter of the pores did not depend on the angle because the distribution of MNP chains did not equal in all samples. Therefore, we modified the particle-dispersion process to try to equalize the distribution of MNP chains in all samples in this study.

## Experimental Results

The particle-dispersion process used ultrasonication. We changed a container of an MNP suspension from plastic to glass vessels to reduce the ultrasonic attenuation and to get well-dispersed MNPs. The other processes for porous resin manufacturing were the same as the previous processes [1]. Fig. 1(a) shows SEM images of the top surfaces of the samples prepared at UV irradiation angles of  $\theta = 30^\circ$ ,  $45^\circ$ , and  $60^\circ$  before MNP removal. Fig. 1(b) shows the relationship between the long diameter of pores and the angle  $\theta$  before and after MNP removal. The long diameter increased with the angle  $\theta$  from  $10.6 \mu\text{m}$  to  $14.8 \mu\text{m}$  before MNP removal and from  $13.8 \mu\text{m}$  to  $19.7 \mu\text{m}$  after MNP removal. The dependence on UV irradiation angle was obtained in the long diameter of pores instead of the pore ellipticity. This result indicates the modification of the particle-dispersion process made MNPs well-dispersed resulting in equalizing the distribution of MNP chains in all samples, thus the long diameter of pores increases with UV irradiation angle.



**Fig. 1** (a) SEM images of the top surfaces of samples prepared at  $\theta = 30^\circ$ ,  $45^\circ$ , and  $60^\circ$  before MNP removal, and (b) relationship between the long diameter of pores and UV irradiation angle before and after MNP removal.

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# **Chitosan-functionalized core/shell nanoparticles for photothermia and magnetothermia against cancer**

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## **Introduction and objective**

Magnetic nanoformulations offer a promising opportunity for the application of hyperthermia as a novel antitumoral approach. The aim of this study is to obtain magnetite (Fe<sub>3</sub>O<sub>4</sub>)/poly( $\epsilon$ -caprolactone) (PCL) nanoparticles (NPs) decorated with chitosan (CS) and to explore its potential in photothermia and magnetothermia.

## **Methods**

(Fe<sub>3</sub>O<sub>4</sub>/PCL)/CS NPs were obtained by a step-by-step procedure (coprecipitation, interfacial polymer disposition and coacervation methods) [1]. DLS, surface electrophoresis and TGA were used for the characterization of the NPs. Hemocompatibility assay was used for assuring a safe parenteral administration and biocompatibility. A broad optimization of the NPs as photothermal and magnetothermal agents was performed.

## **Results and conclusions**

(Fe<sub>3</sub>O<sub>4</sub>/PCL)/CS NPs of  $\approx$  300 nm demonstrated a null toxicity against blood cells. Antitumor hyperthermia temperatures (39 – 42 °C) were observed for both photothermal and magnetothermal approaches. Thus, Fe<sub>3</sub>O<sub>4</sub>/PCL NPs demonstrated a great potential as a photothermal and magnetothermal agents against cancer. Future studies will disclose NPs capacity for *in vivo* combined antitumor therapy.

## **Acknowledgments**

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# POSTER SESSION 1

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Technological Applications



# **Magnetic enhancement of fluorescence in antibody detection based on ferrofluids**

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## **Abstract**

Since the outbreak of atypical pneumonia caused by the severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) which was first reported in December 2019, the novel coronavirus disease (COVID-19) was spreading rapidly and showed a great threat to global public health. In this work, the magnetic field induced self-assembly processes of magnetic microparticles in aqueous liquid (the pure magnetic fluid) and non-magnetic microparticles in ferrofluid (the inverse magnetic fluid) are experimentally investigated. The fluorescence parameters of these self-assembled chain-like microstructures are measured and compared. It is found that the fluorescence in the pure magnetic fluid is weakened, because the scattering and illuminating areas are reduced in the self-assembled chain-like microstructures. On the contrary, the fluorescence in the inverse magnetic fluid is enhanced by the combinational effects of the magnetic dipole force and the magnetic levitational force. The enhancement of fluorescence area ratio of the self-assembled structures exceeds 100% under the effect of the external magnetic field. In the end, a microfluidic chip based on the magnetic field induced self-assembly of nonmagnetic microparticles for antibody detection is proposed, which could improve the measurement accuracy on the concentration of the targeted antibody.

## **Acknowledgments**

This work is supported by the Shenzhen Science and Technology Innovation Commission (Grant No. JSGG20220831101400002) and the National Natural Science Foundation of China (NSFC, Grant No. 91852205), the China Postdoctoral Science Foundation (Grant No. 2022TQ0138), and the Guangdong Basic and Applied Basic Research Foundation (Grant No. 2022A1515110174).

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# Ferrofluid-Gaps for Direct-Drive Wind Turbine Generators

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In a direct drive (DD) wind turbine, there is no gearbox that steps up the rotational speed and steps down the torque produced from the wind by the blades before the mechanical power enters the electrical generator. The elimination of the gearbox results in an increased wind turbine reliability which makes DD a popular choice for offshore installations where maintenance is difficult and expensive [1]. However, due to their low-speed and high-power operation DD generators must cope with enormous torques which result in very large, heavy, and expensive designs that require a substantial amount of permanent magnet material (PMM) [2]. A single 15 MW DD wind turbine, such as the largest commercial models available today, may require approximately 15 tons of high-grade PMM which is both expensive and environmentally damaging to procure. In this PhD project the concept of filling the ‘air-gap’ region between the rotor and stator of DD generators with ferrofluid in order to reduce the amount of PMM required is investigated. A ‘ferrofluid-gap’ would have a greater magnetic permeability than a conventional air-gap, therefore less PMM would be required to achieve the same generator performance [3]. A clear drawback of the ferrofluid-gap concept is an increased mechanical drag within the generator which would result in a decreased efficiency and therefore energy yield of the wind turbine. To evaluate the feasibility of the ferrofluid-gap concept in the context of offshore wind turbines - mathematical modelling methods, multi-physics simulations of ferrofluid-gap flow, and a scaled ferrofluid-gap test generator are being developed with the objective of providing a set of experimentally verified analysis methods that can be used to assess the ferrofluid-gap concept in large-scale generator designs.

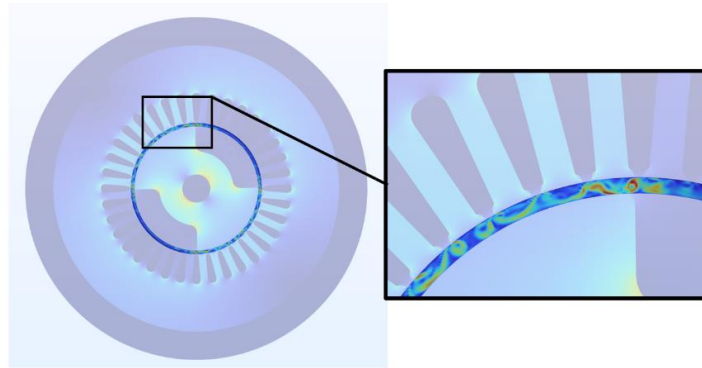


Figure 5: Cross-section of approximate test-rig geometry showing simulated ‘ferrofluid-gap’ flow.

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# **Partial discharge activity in magnetic fluids based on biodegradable oil**

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Changing trends in the field of high-voltage technology demand improvement of insulation properties and heat transfer efficiency regarding sustainable development connected with the usage of environmentally friendly materials. Ferrofluids based on biodegradable liquids stand out as an alternative to mineral oils in the field of liquid insulations for high-voltage equipment. In this paper, the partial discharge (PD) activity in SHELL DIALA S5 BD (biodegradable oil based on gas-to-liquid technology) with iron oxide nanoparticles is investigated. Three ferrofluid samples of various concentrations of magnetic nanoparticles stabilized by oleic acid were prepared, namely a low concentration (0.01%), a medium concentration of (0.1%) and a high concentration (1%). The phase-resolved PD activity was observed under the action of AC high voltage with a frequency of 50 Hz. The experiment allows us to compare the parameters of PD without and with an applied magnetic field made of two permanent magnets which formed a magnetic field with a value of 60 mT at the position of the tip electrode. The results obtained in the absence of the external magnetic field showed that the ferrofluid with the low concentration of magnetic nanoparticles increase the number of measured PDs in comparison to pure oil by around 90 %, however, the average value of charge at positive half-period was more than 3 times lower than in pure oil. At the 0.1 % concentration of nanoparticles number of PDs decreased in comparison to pure oil by around 4 % and the number of PDs decreased to 6 PDs at the highest concentration of magnetite particles. The average value of apparent charge same as the number of PDs decreased with concentration. The applied magnetic field influenced discharge activity at all levels of concentration. The number of PDs decreased by 52 % and 40 % at concentrations of 0.01 % and 0.1 %, respectively. At the highest concentration, the number of PDs decreased from 6 (without magnetic field) to 1 partial discharge after applying the magnetic field. The average apparent charge did not change significantly after applying a static magnetic field.

## **Acknowledgments**

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# Magneto-rheological clutch for variable speed control

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Nowadays the large pumping units installed in several systems operate on wide range domain and under extreme cavitation conditions. Therefore, the operation of large pumping units is strongly affected by cavitation leading to serious mechanical problems and significant maintenance costs. As a result, the service life of large pumping units is diminished and the rehabilitation process targets damaged parts due to expensive cost. A technical solution with the variable speed inducer controlled by a magneto-rheological clutch (MRC) is proposed in patent application no. RO131578-B1/2019 [1] to improve the cavitation behavior. For applications with large pumping units, the MRC provides variable speed control of the output shaft (driven shaft) due to constant rotation of the input shaft (drive shaft). An important constraint for these applications is the geometric limitation in the axial direction between the electrical motor and the hydraulic pump. The disc-type MRC is the best option as it leads to quite good results in terms of weight and compactness [2]. As a result, a disc-type MRC is designed to provide a variable speed of up to 2000 rpm for the driven shaft, while the drive shaft rotates at a constant speed of 2500 rpm. A fixed coil configuration was considered in the design stage to ensure the feasibility of the solution. Then, numerical investigations are conducted to provide an improved magnetic field distribution along the gap filled with magneto-rheological fluid (MRF). Different material properties and several geometrical configurations of the MRC are examined to select the appropriate technical solution. A MRF with improved magneto-rheological behavior under conditions of cyclic thermal stress is specially tailored for this type of applications. The MRC is manufactured by ROSEAL Co. An in-line test rig equipped with a MRC was used to assess its performances. The MRC performances under constant speed drive shaft of 2500 rpm and variable speed range from 2500 to 2000 rpm for the driven shaft were investigated. The temperature distribution in the MRF during the experimental investigations is recorded. The design considerations and experimental investigations on disc-type MRC are underlined.

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# Magneto-rheological brake for underwater applications

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Underwater applications of magneto-rheological fluids (MRFs) are a new field of engineering applications approached. For this reason, many challenging situations occur both in term of MRFs and applications. The greatest advantage of using MRFs is the fast state changing of them. The increasing of the apparent viscosity of such a smart material may be up to 3 orders of magnitude while a moderate magnetic field is applied [1]. Conventional MRF consist of micron sized iron particles dispersed in a base fluid. Nano-micro composite MRFs consist of micron sized iron particles dispersed in a ferrofluid (magnetic nanoparticles dispersed in a carrier fluid). Both MRFs are candidates for applications, but when another liquid medium as water interfere, good immiscibility properties are required [2]. This study focuses on the analysis of two MRF operating in underwater conditions in a magneto-rheological brake (MRB). A conventional MRF132 DG MRF produced by Lord Co. and a nano-micro composite SMR35%Fe+UTR MS 1000G manufactured in our laboratory were selected. The carrier fluid of the MRF is the key ingredient for keeping the two fluids (water and MRF) separate. An in-line test rig equipped with a MRB was used to assess the differences between these two types of MRFs operated underwater conditions. A variable speed range from 100 to 1100 rpm was investigated [3]. An electromagnet was used to induce a variable magnetic field in the proximity of the gap leading to the state changing of the MRFs. The mechanical, electromagnetic and magneto-rheologic torque contributions are studied and the differences between the two MRFs performances are presented. The conventional MRF132 DG exhibit a strong washing away phenomena during experimental investigations leading to a decreasing of the measured magneto-rheological braking torque. The nano-micro composite SMR35%Fe+UTR MS 1000G proves ability of torque control even in underwater applications sustaining a high magneto-rheological braking torque during measurements. This paper extends our developments for underwater application designed for the hydraulic machinery applications [3].

## **Acknowledgments**

Research Project PN-III-P2-2.1-PED-2021-1479(2022-2024)(UEFISCDI) contract no. 723PED2022; Research program LHC-LLM -CFATR(2021-2025)

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# Magnetically tunable electrokinetic instabilities and non-equilibrium patterning of colloidal gradients

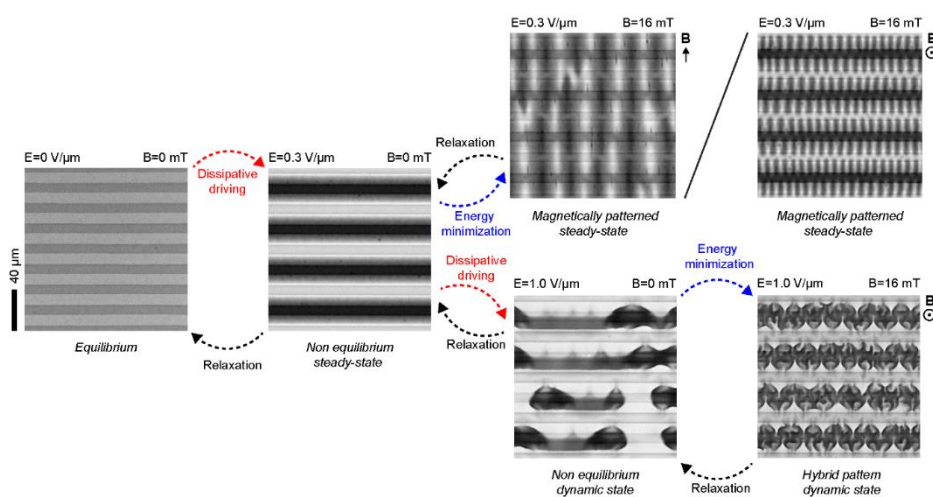
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Non-equilibrium states lead to emergence of novel functionalities that are not achievable in thermodynamic equilibrium, such as self-assemblies and switchable dynamics. Despite their technological importance, designing materials with dissipative functionalities remain challenging since they are inherently complex. Therefore, developing non-equilibrium systems is fundamental. In our recently published work, we introduce a system consisting of electroferrofluid; an electrically and magnetically responsive dispersion of nanocolloids, and demonstrate that steady-state concentration gradients with diffused interfaces can be driven by electric fields in low electric field regimes [1]. We demonstrate the formation of patterns with well-defined periodicities by applying magnetic fields to the voltage-controlled concentration gradient [1].

In addition, in high electric field regimes, stationary undulating patterns, time-varying spatiotemporal states and chaotic behaviors are observed. Furthermore, a wide variety of tunable hybrid non-equilibrium states can be achieved by coupling of electric and magnetic fields, leading to various patterns and structures. Moreover, we demonstrate that minute changes in traces of water modifies the electric responsivity of the electroferrofluid, which can then affect the emerged patterns, which points towards the complexity of the system. This experimental study and the utilized concept of driving hybrid dissipative states by coupling of magnetic and electric fields, bring means and inspiration towards designing materials with adaptive functionalities.



**Figure 1.** Examples of various emerged non-equilibrium states.

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# Evaluation of Tribological Properties of Magnetic Nano-Oil by Ball-on-three-pins Method

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Lubricants have been used as an approach to reduce friction at the sliding surface for long time. Recently, a nano-oils which is the dispersion of nano-particles in lubricating oil has been considered to use as lubricants. Especially, the nano-oil which has magnetism, i.e. a kind of magnetic fluid, is also proposed to use the lubricating oil. We call such a fluid as “magnetic nano-oil” in this study. Although the number of studies on the reduction of the sliding friction by using nano-oil [1] are increasing, a few researches by using magnetic nano-oil [2] has been carried out. In this study, the tribological properties at the sliding surface by application of magnetic nano-oil were evaluated by ball-on-three-pins method using a rheometer which has the function of the friction test (HAAKE MARS iQ Air, produced by Thermo Fisher Scientific Inc.). One test magnetic nano-oil introduced in this abstract is the low viscosity type polyol ester (referred “L-POE”) based magnetic nano-oil (referred “MNO(L-POE)”) produced by Ferrotec Material Technologies Co. The viscosities of base L-POE and MNO(L-POE) are 12 mPa·s and 376 mPa·s, respectively. For applying magnetic field to the sliding surface of the frictional test, the test pieces were made by a plastic magnet which are magnetized and unmagnetized. The surface magnetic field intensity of magnetized one is 100 mT and the magnetic nano-oil is absorbed on the surface of this test piece. The experiments carried out with changing the pressing load and the rotational speed. Figures 1 and 2 show the relationship between the rotational number and the frictional coefficient under 1 N and 10 N of pressing load, respectively. Fig. 1 indicates that the frictional coefficient is larger in order of MNO(L-POE)<sub>mag</sub>, MNO(L-POE)<sub>no mag</sub> and L-POE except for 200 rpm and 400 rpm. If a lubrication area is not considered, this is normal things because viscosity is larger in the same order. However, the frictional coefficient of MNO(L-POE)<sub>no mag</sub> is smaller than that of L-POE for 10 N of pressing load as shown in Fig. 2 and for 200 rpm in Fig. 1. There is the possibility that the inner nano-particles work to reduce the friction. However, for a fair evaluation of these phenomena, the lubrication area should be considered. Other results and the detailed discussion will be presented in the conference.

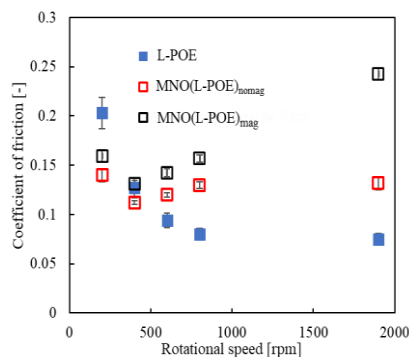


Figure 1 Result of friction test (1 N)

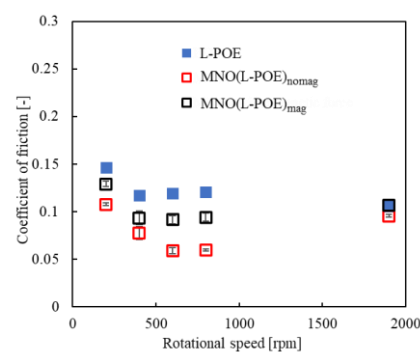


Figure 2 Result of friction test (10 N)

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# POSTER SESSION 2

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*Active systems*



# Dynamics of rotlet's ensemble

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Active systems with chirality are considered in many works (see review [1]). The present work is motivated by the observation of crystals of rotating magnetic droplets under the action of a rotating magnetic field [2]. Since according to experimental observations, the droplets rotate in one plane at some distance from the solid wall we consider a 2D ensemble of rotlets interacting due to induced flows. In dimensionless form the set of equations reads

$$\vec{v}_i = \sum_{i \neq j} \frac{\vec{e}_z \times (\vec{r}_i - \vec{r}_j)}{|\vec{r}_i - \vec{r}_j|^3} . \quad (1)$$

The set of equations (1) describe Hamiltonian dynamics since

$$\frac{dx_i}{dt} = \frac{\partial H}{\partial y_i}, \quad \frac{dy_i}{dt} = -\frac{\partial H}{\partial x_i},$$

where  $H = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$  is an integral of motion. The second integral of motion

$\sum_i (x_i^2 + y_i^2)$  follows from the rotational invariance of the Hamiltonian. Due to these integrals the motion of particles is confined to an area of limited size and they do not come too close to each other. Numerical simulations of an ensemble of  $N$  particles moving according to Eqs.(1) show the following:

- 1) If the only interaction between particles is hydrodynamic, the disordered ensemble of rotlets remains disordered;
- 2) If the repulsion forces are added ( $\vec{v}_i = \lambda e^{-r_{ij}/r_s} \frac{\vec{r}_{ij}}{r_{ij}}$ ) then the ensemble forms a crystal-like structure with hexagonal order;
- 3) If there are two ensembles of rotlets at some distance from each other then initially they rotate around their centre of mass similarly to pointlike rotlets. At later times the ensembles start to exchange particles and finally merge. The resulting disordered ensemble further becomes ordered as shown in Fig. 1

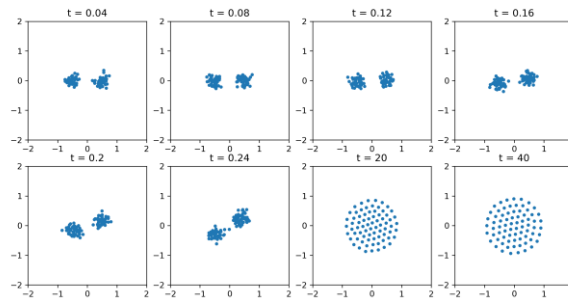


Fig. 1. Merging of ensembles of rotlets  $\lambda = 0.2; r_s = 0.05$

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# Macroscopic emulation of microscopic magnetic particle system

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The investigation of magnetically controllable colloidal system is done by observing the system under microscope and proposing theory for the observed phenomena. Unfortunately, some of the assumptions are hard or even impossible to obtain under microscope (e.g. the orientation of the spherical particle). Therefore, we would like to extend the possible investigation methods with the macroscopic measurements of the magnetic particle systems.

In the present work we focus on the macroscopic measurements of hematite cubes [1] in rotating field. We use cubic magnet which is firmly positioned in the 3D printed cubic shell. To track the orientation of the particle fiducial markers (QR code (ARTag) stickers) are attached to the surface of the shell. The particles are placed in the glycerol-water mixture and magnetic field is generated using coil system. The size of the shell, the orientation of the magnet and the concentration of the glycerol in the mixture are chosen to mimic microscopic hematite cube in the water. The described system allows us to obtain phase diagram of an individual hematite cube in a rotating magnetic field separating regions with rotation on face, edge or vertex

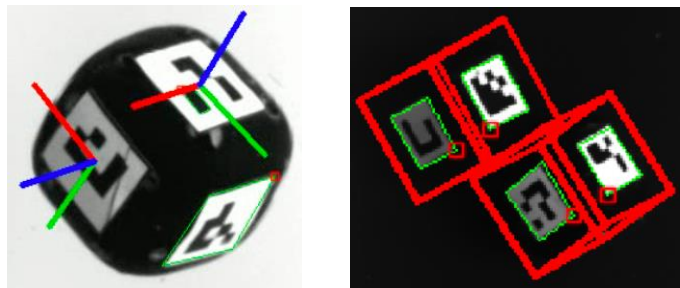
Since the shell is 3D printed, the given method can be extended for the use for any shape and magnetization orientation.

## Acknowledgments

This research is funded by the Latvian Council of Science, PostDocLatvia project No.1.1.1.2/VIAA/3/19/562 and project BIMs, project No. lzp-2020/1-0149.

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# Magnetorheological gradient pinch mode valve

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## Introduction

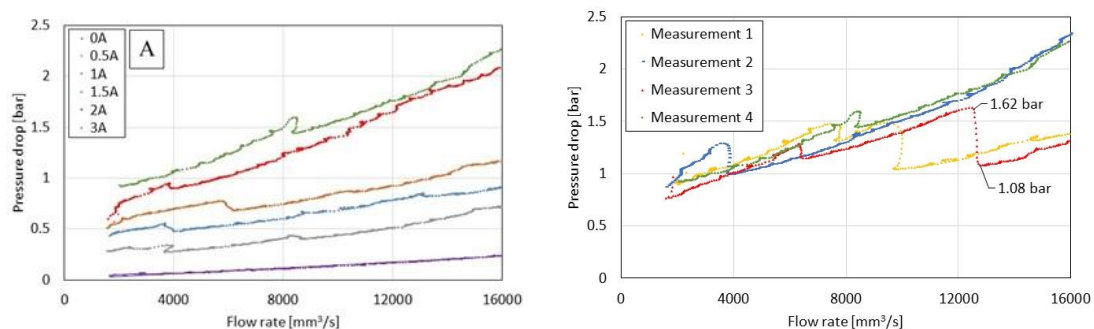
Magnetorheological (MR) fluid is a suspension of ferromagnetic micro-size particles in a carrier fluid. MR fluids can operate in four working modes: valve, shear, squeeze and gradient pinch. MR fluid is usually exposed almost homogeneous magnetic field. However, the gradient pinch mode is different because magnetic field distribution is highly non-uniform. In 2008, Carlson et al. [1] patented an MR valve operating in pinch mode. This team described a method of varying the effective diameter of a flow channel by the magnetic field (change flow curve slope). The information about pinch mode is limited. This paper aims to present the MR valve measurement working in pinch mode.

## Materials and methods

The authors developed a single-gap MR pinch mode valve with a thru-hole channel ( $D = 3$  mm). This valve was located in a test rig with a floating piston. The dynamometer imposes the motion of a floating piston through the channel. The pressure drop and floating piston position (flow rate) were monitored. The commercially available MR fluid MRF-122EG was used for experiments.

## Results and conclusion

Figure 1 left shows the increase in the slope of the flow curve and the offset change with the increase in the magnetic field. This is consistent with the results [1]. However, the flow curve showed significant instabilities (unexpected pressure drops). Figure 1 right shows the repeatability of the measurement for electric current 3 A. It is evident that the repeatability is relatively poor due to abrupt pressure variations. This is probably due to the clusters of particles being washed out from the active zone.



**Figure 1** Flow curve of MR pinch valve (left); repeatability of experiments (right)

## Acknowledgements

The authors wish to acknowledge the kind support of the projects: GACR 21-45236L and 2020/39/I/ST8/02916.

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# Hydrogel-based soft actuators with fast motion under magnetic stimulus

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## Abstract

Soft actuators are materials capable of responding with motion, or with changes in some of their dimensions, to different types of stimuli, such as changes in temperature, pH or the application of a magnetic field. The former represents one of the most attractive stimuli because magnetic fields are easy to use, present a fast response and safe penetration in biological environments.<sup>1,2</sup> In this work we studied how the formation of magnetic particle chains within polymeric matrices influences the response of the actuators to the application of an external magnetic field. This study was carried out by studying the microstructure of the actuators using microCT techniques, and by analysing the response of actuators with the same shape, but with or without the particles aggregated into chains. The torsion of the actuators was also studied as a function of the structures formed by the particle chains within the polymeric structure, differentiating in this work two types of structures: i) circularly-structured and ii) helically-structured magnetic composites.

## Acknowledgments

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# Bidirectional flow in ferromagnetic ferrofluids in an AC magnetic field

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Stable suspensions of magnetic nanoplatelets in anisotropic fluids, such as nematic liquid crystals, exhibit ferromagnetic behaviour [1]. Similar ferromagnetic fluids can be achieved also as suspensions of magnetic nanoplatelets in isotropic alcohol, provided the nanoparticle concentration is high enough. Here we report on investigations of such ferromagnetic ferrofluids, prepared as suspensions of scandium substituted barium-hexaferrite nanoplatelets in tert-butanol [2], in the presence of an alternating external magnetic field. When observed with polarisation microscopy, regular and periodic bright and dark stripes perpendicular to the magnetic field form and the stripes are recognised as magnetic domains. Even more intriguingly, we observe flow along the stripes. The flow, which is visible as transport of particles, was studied more accurately by performing space-time correlation spectroscopy of thermally excited fluctuations. We measured the velocity profile along the stripes and noticed that the velocity is the largest in dark regions, which represent domain walls, reaching the values of several  $\mu\text{m/s}$ . A possible explanation of the origin of the observed flow will be given.

## Acknowledgments

The authors acknowledge funding from the Slovenian Research Agency P1-0192, J1-2459 and BI-AT/20-21-020.

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# From equilibrium properties to self-propulsion of active multicore particles

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Magnetic multicore nanoparticles (MMNPs) are clusters of single-domain magnetic nanocrystals embedded in a polymer or other non-magnetic rigid matrix [1]. Grains (magnetic nanocrystals) have a typical diameter about 10 nm, the size of MMNPs can range from tens to a few hundred nanometers. Recently, MMNPs have attracted a lot of scientific attention due to their wide range of potential biomedical and biotechnological applications including magnetic particle imaging, drug delivery systems and magnetic hyperthermia cancer treatment.

Using Langevin dynamics simulations in ESPResSo package [2], we model MMNPs as spherical impenetrable particles filled randomly and uniformly with spherical magnetic grains. Each grain has a magnetic moment of constant magnitude which can either freely rotate under the action of applied magnetic fields and thermal fluctuations, or has a finite magnetic anisotropy, thus, to fluctuate it needs to overcome a given energy barrier. All grains interact with each other via the dipole-dipole interaction potential.

To study the equilibrium self-assembly of MMNPs in the absence of an applied field, we carried out a cluster analysis of MMNP dispersions with different values of dipole-dipole interaction constants. The cluster analysis was performed at two levels: both the self-assembly of MMNPs and the self-organization of grains inside the resulting clusters of MMNPs were studied. We calculated such characteristics as the size distribution of MMNPs clusters, the number of bridges formed by grains from different MMNPs in clusters of various sizes, the length of bridges, the number of particles in bridges, and magnetic characteristics also. It has been shown that for the formation of stable MMNPs clusters, the existing of bridges formed from neighboring MMNPs is necessary condition. The analysis of the bridges showed that there is a bimodal distribution of their topology: small clusters, similar to linear chains, and clusters made up of a large number of grains, resembling an open ring, with a very small magnetic moment.

To assign self-propulsion on MMNPs, we apply constant force to the particle centre of mass, creating Brownian swimmers [3]. We study the ability of such particles to propel in the field direction depending on the internal anisotropy of grains, field-particle coupling and eigen propulsion velocity.

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## Short hematite chains

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At room temperature hematite is a weak ferromagnetic material with an unorthodox magnetization orientation, thus hematite colloids represent a unique system to study interactions between two particles [1]. In scientific literature several experiments can be found with such colloids and particularly interesting are experiments by Soni et al. [2] where they show that a two-dimensional chiral fluid can be created using hematite colloids with cubic-shaped hematite particles in rotating magnetic field.

Swarming experiments [3] of micron-sized hematite cubes in a rotating magnetic field show that swarms and therefore chiral fluid consist of short interacting hematite chains. Therefore, to better understand this phenomena here we look at building blocks, i.e. short hematite chain behavior in rotating and static magnetic field. We find equilibrium structures of chains in static magnetic field and oversevere chain dynamic in rotating magnetic field. We find and experimentally verify that tree motion regimes are possible: solid body rotation, back-forth motion, chain break and assembly.

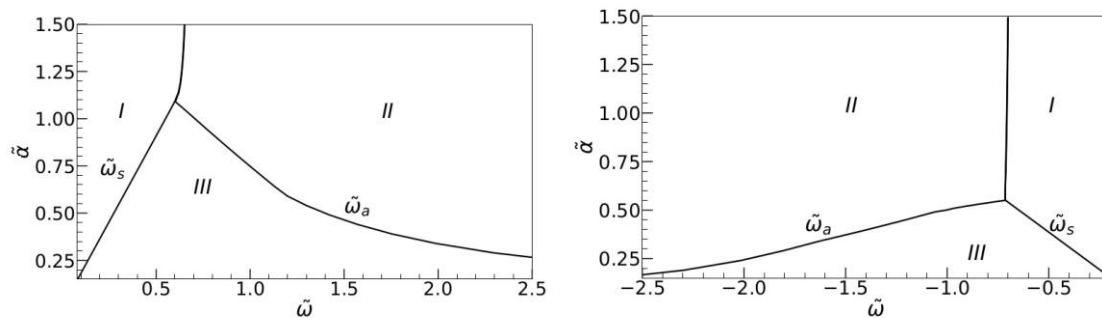


Figure 1. Borders of long-time dynamics regimes.

### Acknowledgments

This research is funded by the Latvian Council of Science, PostDocLatvia project No.1.1.1.2/VIAA/3/19/562.

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# **Dynamical pattern-formation and transport in a low-concentrated magnetorheological fluid under sinusoidal fields**

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The transport processes and dynamical pattern formation of clusters of magnetic particles in a low-particle concentration magnetorheological fluid under the influence of a superposition of two perpendicular sinusoidal fields is studied experimentally. By varying the frequency and phase shift to the perpendicular fields, we are able to experimentally analyze a wide range of field configurations, including the case of a pure rotating field and the case of an oscillating unidirectional field. The fields are applied parallel to the horizontal plane where the fluid lies or in the vertical plane. For fields applied in the horizontal plane, we observed that, when the frequencies ratio increases, the average cluster-size exhibits a kind of periodic resonances. When the phase shift between the fields is varied, the average chain-length reaches maximal values for the cases of the rotating field and the unidirectional case. We analyze and discuss these results in terms of a weighted average of the time-dependent Mason number. In the case of a rotating field on the vertical plane, we also observe that the competition between the magnetic and the viscous forces determines the average cluster size. We show that this configuration generates a series of physically meaningful self-organization of clusters and transport phenomena.

## **Acknowledgments**

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## Stimuli-responsive nanoparticles within liquid-liquid phase separation droplets.

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One of the challenges in the field of droplet technology is the practical manipulation of droplets without physical contact. One potential solution to this problem would be to compartmentalize field-responsive nanoparticles within the droplet microarchitecture. Our goal here is to confine magnetite and gold nanoparticles in specific subsites within droplets not only to make them field-responsive, but also to create an asymmetric response to external fields and/or allow for field-induced reconfigurability. We select magnetite and gold nanoparticles that respond to external magnetic fields and laser irradiation, respectively. The strategy focuses on preparing water-in-oil droplets with internal phase separation and partitioning of nanoparticles in each subphase. This is achieved through mixing solutions of polyethylene glycol (PEG) and dextran as the aqueous phase of the droplets. At specific concentrations, these two polymers phase-separate resulting in Janus-shaped droplets [1]. To compartmentalize gold and magnetite nanoparticles within the PEG- and dextran-rich phases, gold nanoparticles covered with PEG-thiol polymer and magnetite nanoparticles functionalized with dextran polymer [2] are synthesized to enable preferential encapsulation within PEG-rich and dextran-rich phases, respectively. To demonstrate the response of these droplets to external fields, we perform experiments where heat is generated by application of alternate magnetic fields (i.e., hyperthermia) and/or laser irradiation (i.e., photothermia) to test for potential synergistic heating capability by the gold and magnetite domains within the droplet. We also observe the internal reconfigurability of the droplets induced by temperature changes, and self-healing ability by using an optical microscope. Through this approach, we have demonstrated the tunable confinement of field responsive nanoparticles within microdroplets, their response to the application of external fields, and heat-induced reconfigurability, which have the potential for application in fields such as active matter or microreactor technology.

### Acknowledgments

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# Formation of micropatterned hydrogels based on magnetic Pickering emulsions

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## Abstract

The construction of hybrid microstructured complexes based on hydrogels and functional micro-compartments (such as micro-sized droplets or capsules) is expected to lead to a new generation of materials, which could find applications in fields such as soft robotics or micro-actuators [1]. Controlling the spatial distribution of micro-compartments within hydrogels is particularly interesting, because it would enable spatial modulation of the functions provided by the compartments (e.g., chemical reactions). In this regard, the use of Pickering emulsion droplets (i.e., stabilized by solid particles that adsorb at the oil/water interface) as microcompartments is especially relevant, because the particles can be chosen to guide the droplet spatial positioning. In particular, magnetic Pickering emulsion droplets (MPED) can respond to magnetic force fields [2]. Here, we demonstrate the formation of hydrogel drops equipped with MPED as integral compartments of their microstructure, which can be organized according to pre-set patterns by using magnetic fields. For this purpose, oil-in-water MPED stabilized by magnetite nanoparticles functionalized with oleic acid have been used. We employed a gel precursor as the external phase of the MPED, which allows crosslinking of the MPED-containing hydrogel. Before gelation is completed, the arrangement of the MPED within the hydrogel is achieved thanks to spatially modulated magnetic fields generated by microstructured stamps [3]. In this way, depending on the stamp pattern, we can produce microstructured hydrogels with different geometries, which would enable their use as smart materials in applications like those listed above.

## Acknowledgments

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# POSTER SESSION 2

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Environmental Applications



# Particulate removal and ozone generation in magnetic fluid air filter using electrostatic force

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## Abstract

Air pollution is one of the serious environmental issues. Particulate matters (PMs), which are emitted from fossil fuels-based energy conversion devices such as diesel engines and boilers, cause the air pollution. PMs are composed of carbon soot and sulfur trioxide. These PMs have a significant impact on the air pollution. Therefore, air purification technologies including PM collection are needed. There are some types of filtering techniques. One example is a high efficiency particulate air (HEPA) filter. HEPA filter is the most efficient air filter. However, the pressure loss is an essential problem (maximum initial pressure loss is 245 Pa). Another one is an electrostatic precipitator (ESP). This filter is effective for wide-range size particles. However, it is known that re-entrainment occurs in an ESP, because the carbon has low electronic resistance [1]. To solve these problems in these filters, a magnetic fluid filter that uses a magnetic fluid and an electrostatic force has been proposed and developed [2]. Fig. 1 shows the principle of the magnetic fluid filter. The magnetic fluid is fixed by magnets. A magnetic fluid is a colloidal solution and react the magnetic field. An AC or DC high voltage is applied to the electrodes. Then, the electrostatic force occurs between the magnetic fluid and the upper electrode. PMs in the air flow are collected on the surface of magnetic fluid by the electrostatic force. The PM collection efficiencies and ozone concentration generated are discussed.

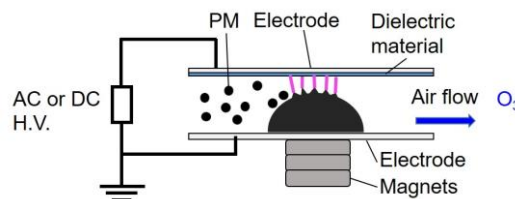


Fig. 1 Principle of magnetic fluid filter.

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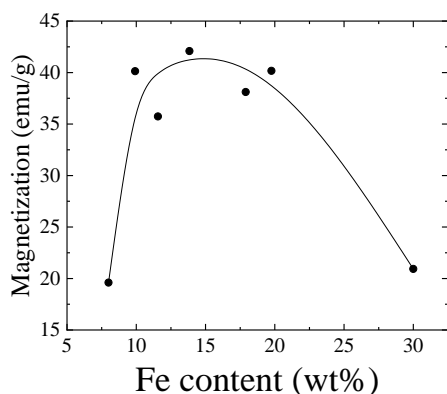
# Magnetic carbon nanocomposites with improved magnetic response

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Nowadays, the environmental state of the water that flows through our rivers and pipelines has gained extensive attention. Some of the most challenging pollutants to remove include phenolic and other aromatic organic compounds. The use of magnetic carbon nanoadsorbents allows not only the magnetic separation of the adsorbent from the aqueous media, but also its reuse in various decontamination cycles. The combination of adsorption and photocatalysis improves the pollutant removal from the aqueous media, avoiding secondary contamination [1].



**Figure 1.** High field magnetization of the Fe-C nanocomposites as a function of wt%Fe

In this work, the synthesis of magnetic carbon nanocomposites were obtained from the thermal decomposition of fructose, employing  $\text{FeCl}_3$  as iron precursor [2]. The structural characterization (X-ray diffraction, Transmission Electron Microscopy, TEM) indicate the formation of  $\alpha\text{-Fe}$ ,  $\text{Fe}_3\text{C}$  and graphitic carbon (matrix) phases at high annealing temperatures ( $T_{\text{ann}} \geq 800$  °C). The magnetic properties, characterized through SQUID magnetometry, confirms the phase distribution. Maximum values of the saturation magnetization (magnetization at 6 T) around 42 emu/g are found for  $10 < \text{wt}\% \text{Fe} < 20$  (Figure 1). Further increase in

the Fe content provides a sharp decrease in the magnetization ascribed to the formation of Fe oxides. Nanocomposites presenting high magnetization values have further been attached photocatalytic anatase  $\text{TiO}_2$  onto their surface [1]. The photocatalytic response for phenol degradation of the resulting nanocomposites was characterized employing a 300 W Xenon lamp. Results showed an effective depolluting power in these nanocomposites, as a result of the combined adsorption of carbon and the photocatalytic activity of the  $\text{TiO}_2$ .

## Acknowledgments

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# Thermoelectric coefficient dependency on chemical composition of ionic liquid based ferrofluids

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In recent years, complex fluids are attracting attention as an alternative thermoelectric (TE) material. Unlike in solids, several inter-dependent TE effects take place in such fluids; most notably, the electrochemical (thermogalvanic) reactions of redox salts, the thermodiffusion of charged species and the electronic double-layer formation of ions near the electrodes. They possess Seebeck (or temperature) coefficient values that are generally an order of magnitude larger, and are made of cheap and abundant raw materials compared to the semiconductor counterparts, their TE power-output remains quite low with a limited operational temperature range (e.g., 100 °C). To this end, ionic liquids with high ionic conductivity and boiling points (e.g. > 200 °C) are auspicious candidates to overcome these issues. Additionally, the inclusion of highly charged colloidal nanoparticles has been shown to further enhance the Seebeck coefficient and the power output by proper tailoring [1]. In this work, the thermoelectric properties of ionic liquid (EMI-TFPI) based maghemite ferrofluids with tris(2,2'-bipyridine) [Co(bpy)<sub>3</sub>]<sup>3+/2+</sup> redox couple were studied with varying combinations of NP surface coating molecules and counter-ions. The results shed light upon the intricate balance between the NP concentration and the solvation shell of redox salts affecting the fluids' overall TE energy conversion process and performance. A discussion on some key experimental parameters for improving the efficiency of liquid thermoelectrochemical cells will also be given.

## Acknowledgments

This work received partial funding from: ANR TEFLIC (grant number ANR-12-PRGE-0011-01), LabEx PALM (ANR-10-LABX-0039-PALM), the European Union's Horizon 2020 research and innovation programme under the grant agreement n° 731976 (MAGENTA) and CAPESCOFECUB n714/11 & PICS-CNRS n5939 Campus France.

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# POSTER SESSION 2

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Physical Properties



# **Comparison of physical properties of ferrofluids based on mineral transformer oil and biodegradable gas-to-liquid oil**

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Ferrofluids based on mineral transformer oil have been intensively studied over two decades owing to their promising thermal and electrical insulating properties. However, current environmental demands on transformer operation give priority to the use of biodegradable transformer oils. Clearly, the differences in physical properties of biodegradable oils and those refined from crude oil determine the physical properties of ferrofluids based on the two types of oils. In this study, ferrofluids with various concentrations of iron oxide nanoparticles have been prepared on two oils, mineral transformer oil Mogul Trafo CZ-A (M-samples) and biodegradable transformer oil Shell Diala S5 based on gas-to-liquid technology (S-samples). The ferrofluids were subjected to experimental investigation of magnetization, AC magnetic susceptibility, thermal conductivity, viscosity and dielectric response. Based on zero-field-cooled and field-cooled magnetization curves, a lower temperature at a specific magnetization maximum associated with the melting of the oil (phase transition) was found for M-samples than for S-samples. The effect of carrier liquid on the potential transition from extrinsic to intrinsic superparamagnetism is qualitatively discussed. Spectra of AC magnetic susceptibility of both types of ferrofluids exhibit identical behavior. The viscosity of M-samples is remarkably higher than that of S-samples. On the other hand, M-samples exhibit lower thermal conductivity than S-samples. In both cases, the thermal conductivity linearly decreases with temperature. Dielectric spectroscopy has revealed remarkable dielectric dispersion below 100 Hz in both ferrofluid types. The relaxation has been ascribed to interfacial polarization, which can be considered as a serious drawback from an electrical engineering application point of view. The measured physical properties of the ferrofluids are analyzed in regard to the density and viscosity of the base oils.

## **Acknowledgments**

This research was funded by the Slovak Academy of Sciences and Ministry of Education in the framework of project VEGA 2/0011/20, 1/0154/21 and Slovak Research and Development Agency under the contract No. APVV-18-0160.

# Optical properties of nanofluids based on goethite ( $\alpha$ -FeOOH) nanorods under magnetic field

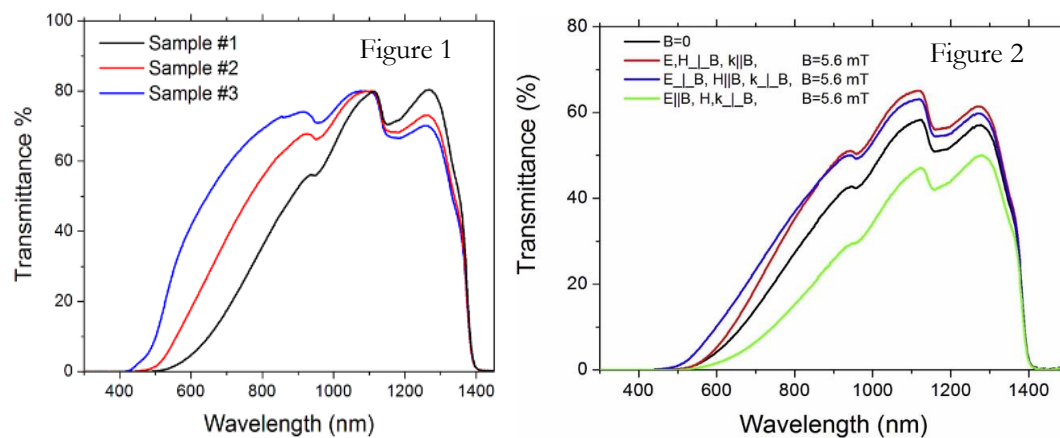
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We show how polarized optical properties of aqueous colloidal suspensions of goethite ( $\alpha$ -FeOOH) nanorods, prepared with different methods, depend on an applied magnetic field. In particular, the transmittance in the near-infrared range can be tuned by changing magnetic field direction and strength. This effect is strongly connected to the nanoparticles morphology, which, in turn, depends on the preparation method.

The considered samples are: Sample #1, prepared by adding dropwise 5 mL of 0.06 M Fe(NO<sub>3</sub>)<sub>3</sub> solution to 45 mL of 1.5 M NaOH solution; Sample #2, prepared as #1, except for the use of 35 wt% TEAH water solution instead of NaOH and Sample #3, prepared by adding all at once 35 wt% TEAH water solution. They showed different sizes and morphologies [1]. Figure 1 shows their transmittance spectra. Sample #1 was the most sensitive to an applied magnetic field [2]. Figure 2 shows its transmittance spectra, under an applied field of 5.6 mT and different relative polarizations of the input beam (whose electric/magnetic field directions are represented in Fig. b as  $\mathbf{E}/\mathbf{H}$ , respectively) with respect to the external magnetic field direction ( $\mathbf{B}$ ) and optical beam propagation vector ( $\mathbf{k}$ )



These results show that the optical properties of goethite-based suspensions are very sensitive to even weak external magnetic fields, with promising perspectives for sensing applications.

## Acknowledgments

NEST-Network 4 Energy Sustainable Transition (PNRR Partenariato Esteso PE0000021) for partial support. Dr. S. Barison, Dr. F. Agresti (ICMATE-CNR, Italy) for Sample #1.

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# New Pickering emulsion systems based on magnetic particles

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In numerous industrial and medical applications, there is a crucial need to use emulsion systems with good stability that can be resistant to aging processes, including the coalescence of droplets. One of the strategies is to use solid particles as stabilizers. Such particle-stabilized emulsions are referred to as Pickering emulsions. Particles can adsorb into the interface between the continuous and dispersed phases of emulsions *via* capillary forces and form a shell around droplets. The layer of particles acts as a mechanical barrier against coalescence and provides the kinematic stability of the emulsions. The possibility to tune the emulsion properties with a suitable choice of particles and synthesis procedure give us plenty kinds of unique Pickering emulsions. From this point of view, the magnetically modified Pickering emulsions are very interesting. Zhou *et al.* [1] demonstrated that the reaction rate of Pickering emulsion was significantly enhanced with bacterial magnetic particles as nanoscale magnetic stirring bars, which can be encapsulated into each micro-droplet. We aim to develop new Pickering emulsions using magnetic nanoparticles isolated from the magnetotactic bacteria *Magnetospirillum magneticum*. These bacteria contain chain-like magnetite nanoparticles called magnetosomes. Magnetosomes have been an interesting material in the field of magnetic hyperthermia for a long time [2] as the high shape anisotropy improves their response to the applied magnetic field. The idea is to modify magnetosome chains by mechanical forces (in the sonication process) and study the impact of the number of magnetosomes per chain on the stability and magnetic properties of such Pickering emulsions. The motivation to synthesize systems originates from the effort to tune the heating effect in the condition of rotating and oscillating high-frequency magnetic fields. The preliminary results for the heating efficiency of new magnetic Pickering emulsions show the specific absorption rate values in the range from  $15 \text{ W}\cdot\text{g}^{-1}$  to  $40 \text{ W}\cdot\text{g}^{-1}$  at  $16.2 \text{ kA}\cdot\text{m}^{-1}$  and 356 kHz depending, for example, on the preparation conditions. These values are very promising from the point of application of new Pickering emulsion in all areas of hyperthermia treatment.

## Acknowledgments

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# Diffraction of Laser light by a Ferrocell and ferrofluid layers: A comparison

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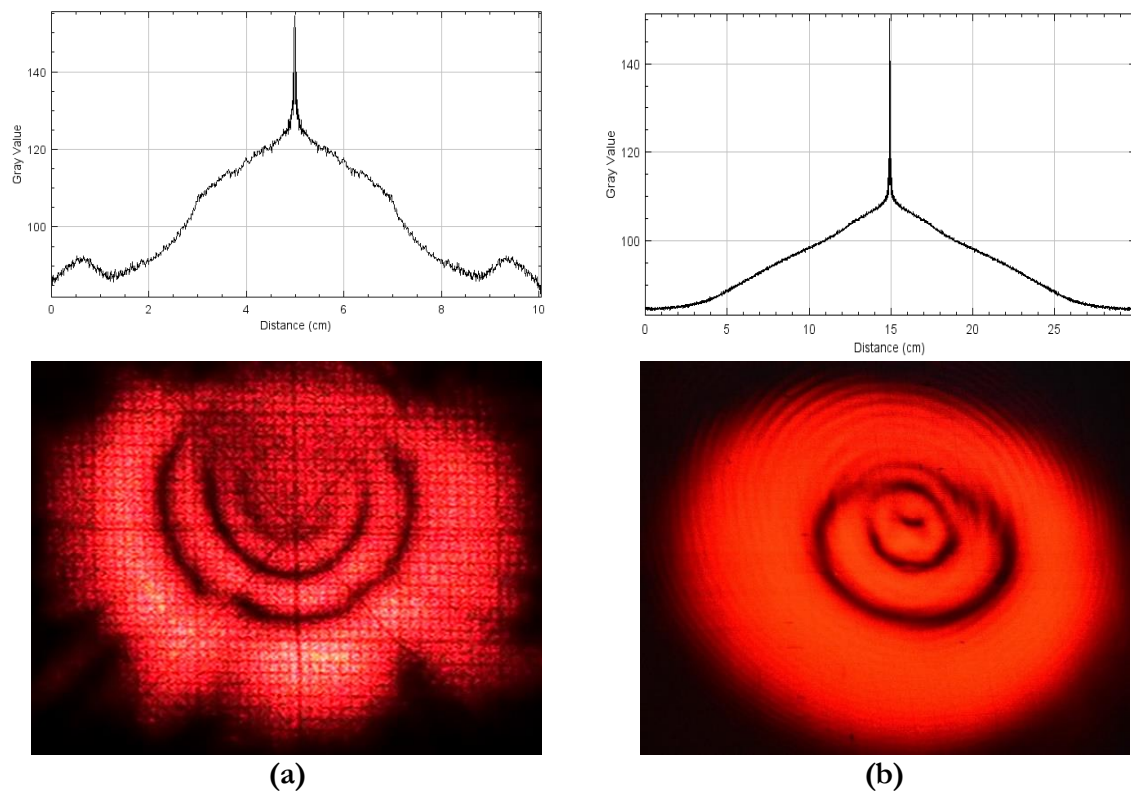
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## Abstract

In an earlier paper, we compared extinction induced in ferrocell and ferrofluid layers [1]. Here, we report similar study for diffraction of light. We have studied static magnetic field-induced diffraction in both cases. It is found that there are different. Similarly, the power spectra of diffraction patterns are also quite distinct. The intensity of the peak of the spectra of ferrocell is sharper and larger compared to that of ferrofluid. One representative pattern is shown in Figure 1. The temperature variation of the patterns is also investigated. Results are analysed.



**Figure 1.** Power Spectrum along with Diffraction patterns in zero fields [(a) Ferrofluid (b) Ferrocell].

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## Anisometric magnetic nanoparticles in nematics

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Liquid crystals are doped with various particles in order to improve their already outstanding properties and prepare materials for new applications. It is known that properties of nanoparticles, such as size, shape, magnetic and electrical properties, surfactant, etc. significantly modify response of liquid crystals to external stimuli. The aim of inserting magnetic nanoparticles is to prepare composites responsive to small magnetic fields and thereby enable their technical applications.

We report about the influence of hematite [1] and goethite [2] nanoparticles of anisometric shape on sensitivity of nematic liquid crystal to magnetic field. Hematite spindles order perpendicular to an applied magnetic field and goethite lath-like nanoparticles orient parallel in magnetic field smaller than critical  $H_c$  and perpendicular in magnetic fields larger than  $H_c$  (see Figure 1). Capacitance measurements showed a decrease in threshold magnetic field of Fréedericksz transition for composites with three lengths of hematite nanoparticles ( $\sim 200$  nm,  $\sim 300$  nm,  $\sim 400$  nm) and revealed response in small magnetic field region below threshold. Two types of samples were prepared with goethite nanoparticles – compensated with zero initial magnetization and magnetized with nonzero initial magnetization. For theoretical description of the experimental data the continual theory was modified. Experimentally observed shift to higher magnetic field for compensated composite and to lower magnetic field for magnetized composite is in very good qualitative and quantitative agreement with the developed theory.

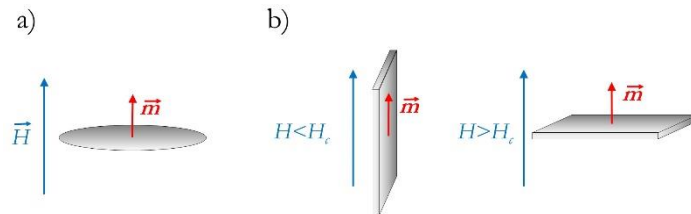


Figure 1: A schema of a) spindle and b) lath-like nanoparticles in magnetic field.

### Acknowledgments

This work was supported by the Slovak Academy of Sciences, in the frame work of project VEGA 2/0043/21.

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# Magnetic field dependence of the magnetic dynamics of BaHF nanoplatelet suspensions

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Tuning the macroscopic properties of ferrofluid suspensions enables a multitude of applications. In order to achieve that, it is of uttermost importance to understand the microstructure, reflecting the nanoscale characteristics of the suspensions. Following the theoretical prediction of a fluid ferromagnet more than 50 years ago, it only recently has been shown that even in suspensions of ferrimagnetic barium hexaferrite (BaHF) nanoplatelets in isotropic n-butanol colloidal nematic phases can form [1-3]. In order to understand the self-assembly mechanism stabilizing the order, an analysis of the interactions involved is necessary.

Studying the magnetization dynamics in BaHF suspensions in n-butanol, we found that multiple relaxation modes can appear in the complex susceptibility spectrum. Given the fact that these modes cannot be described by a single Debye-type mechanism we attribute them to a superposition of single particle relaxation at high frequencies and low-frequency relaxation of self-assembled structures [4,5].

Varying the amplitude of the probe field and applying an external static bias field, either parallel or perpendicular to the excitation direction, we demonstrate selective manipulation of the mode structure of the spectra. Depending on the field geometry and its strength, particular modes can be suppressed or/and shifted in the frequency domain. Analyzing the effects of parallel and perpendicular bias fields allows us to comprehend the nature of the self-assembly mechanisms underlying the collective dynamic behavior. We apply theoretical models to describe the findings quantitatively.

## Acknowledgments

This work was funded by DFG, projects NA 1668/1-1, LU 800/7-1 and by ARRS, projects P1-0192, P2-0089, J1-2459, J7-8267.

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# Experimental ultrasound technique for magnetorheological fluids settling measurement

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## Abstract

Magnetorheological fluids (MRFs) present an instantaneous and reversible change in their rheological properties in response to a magnetic field. However, these materials present a main drawback that has limited the application and industrialization of these devices, their poor gravitational stability.

Several researchers have centred their investigation in the characterization and improvement of the gravitational stability of MR fluids [1]. However, all the developed methods present some limitations in terms of maximum allowable particle concentration, precision, development feasibility or the risk of inducing changes in the thermo-physical properties of the fluid itself.

This work presents a new experimental method based on ultrasound for determining the stability of magnetic fluids. The development of this procedure implies the choice of the optimal set-up; the acquisition and processing of data; and the correlation of the ultrasonic waves' transmission speed with magnetic fluid gravitational stability. Through the new technique, the stability of different formulated MR fluids has been evaluated.

The results indicate that the new procedure is versatile and effective in measuring the concentration of particles in suspensions. It has been shown to work with concentrations of up to 30% in volume of solid fillers and is suitable for measuring a wide range of particle sizes, from 50 nm to 1.09  $\mu\text{m}$ , both in the nano- and micro-metric scale. A calibration curve has been developed to measure the sedimentation of the suspension over time and the system has been found to have high repeatability and insensitivity to adjustment parameters. Additionally, it has potential application in measuring the gravitational stability of non-magnetic colloids.

## Acknowledgments

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# Dynamics of liquid magnets in a rotating magnetic field

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A combination of the shape-anisotropy of magnetic nanoplatelets (MNP) with magnetic and electrostatic interactions give rise to a fascinating new system – liquid magnets. Those systems, recently demonstrated by Mertelj et al., combine fluidity with spontaneous ferromagnetic order [1, 2].

Strong interparticle correlations profoundly affect the dynamics of the MNPs, which is still not fully characterised. Here, we explore the magnetisation dynamics and the magnetomechanical effect of a colloidal dispersion of barium hexaferrite nanoplatelets suspended in 1-butanol in rotating magnetic fields. At low volume fractions, the system is isotropic and becomes ferromagnetic liquid crystal above a critical concentration. The magnetic response is distinguished by several relaxation modes with non-Debye behaviour reflecting the high polydispersity of the suspensions and the intricate interactions affected by the ionic surfactant in the system. Field-induced self-assembly of the magnetic nanoplatelets tuned by the surfactant-mediated electrostatic interactions strongly affects the emergence of the low-frequency modes in the magnetic spectra as well as the field-induced birefringence in the system. Using the torsional balance, we measure the magnetomechanical torque induced in a rotating magnetic field as a function of the field amplitude and frequency. The direct comparison between the magnetic and magnetomechanical spectra allows us to unveil the role of self-assembly and the magnetohydrodynamic flow on the momentum transfer. Here we show that the development of the nematic order can be observed from the growth of the collective modes in the magnetic, mechanical and optical responses.

## Acknowledgments

This work was funded by DFG, projects NA 1668/1-1, LU 800/7-1 and by ARRS, projects P1-0192, P2-0089, J1-2459, J7-8267.

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# Influence of an ionic surfactant on the collective dynamics of magnetic nanoplatelets

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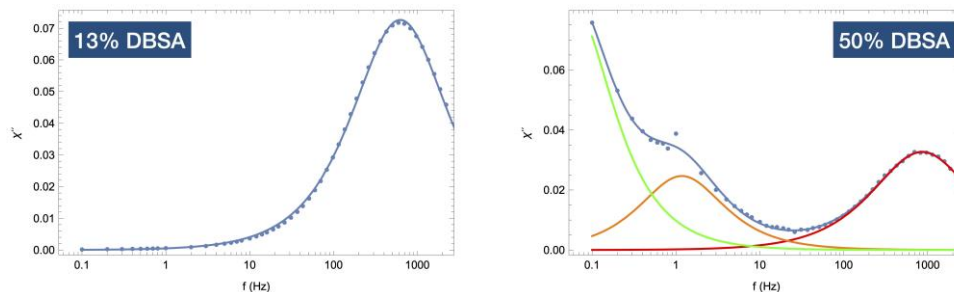
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Since the discovery of ferromagnetic nematic liquid crystals [1], suspensions of anisotropic scandium-doped barium hexaferrite (BaHF) platelets in anisotropic and isotropic hosts deliver astonishing new insights into the dynamical nature of this system. To balance the strong magnetic dipolar and steric interactions, a duly powerful electrostatic stabilization is provided by the anionic surfactant (DBSA) to avoid aggregation of the platelets in an isotropic medium [2]. In the latter system, we performed AC susceptibility measurements to investigate the magnetic dynamics of the system and found that collective modes can be induced or suppressed in several ways [3, 4]. Here we explore how a variation of the surfactant concentration can give rise to multimodal structures in the AC susceptibility spectra even at low magnetic particle concentration. We attribute the emergence of low-frequency peaks to the correlation of the platelets, which is enhanced by increasing the DBSA concentration due to the growing ionic strength in the suspension.



**Fig. 1.** Single mode AC susceptibility spectrum of BaHF suspension with 13% DBSA (left) and multimodal spectrum with 50% DBSA (right).

## Acknowledgments

This work was funded by DFG, projects NA 1668/1-1, LU 800/7-1 and by ARRS, projects P1-0192, P2-0089, J1-2459, J7-8267.

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# Microstructural, magnetic and dielectric properties of La<sup>3+</sup> ion doped Mg<sub>0.5</sub>Ni<sub>0.5</sub>Fe<sub>2-x</sub>La<sub>x</sub>O<sub>4</sub> (0 ≤ x ≤ 0.1) ferrite nanoparticles for microwave absorption application

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## Abstract

A series of La<sup>3+</sup> ion doped magnesium nickel ferrites, Mg<sub>0.5</sub>Ni<sub>0.5</sub>Fe<sub>2-x</sub>La<sub>x</sub>O<sub>4</sub> (0 ≤ x ≤ 0.1) of a cubic spinel structure were prepared by the co-precipitation method. Various characterization techniques, including XRD, HR-TEM, EPR and VSM were used to investigate structural and magnetic properties. The lattice constant increases with La<sup>3+</sup> ion concentration owing to the substitution of larger ionic radii La<sup>3+</sup> at the lower ionic radii Fe<sup>3+</sup> ions site. The average crystallite size and lattice parameter are in the range of 12-7 nm and 8.348-8.361 Å respectively. The particle size estimated by HRTEM is comparable to that estimated by XRD analysis. Analysis of EPR spectra states that, when the concentration of La<sup>3+</sup> ions increases, the spin-spin relaxation period increases from 5.936 x 10<sup>-11</sup>s to 7.427 x 10<sup>-11</sup>s. g-value with La<sup>3+</sup> ion addition decreases from 2.57 to 2.12. The saturation magnetisation and the coercivity decrease with increasing rare-earth content. M-H hysteresis loop shifts from a ferromagnetic to a superparamagnetic nature with La<sup>3+</sup> ion addition. The lower value of squareness, less than 0.5 suggests fewer magnetostatic interactions among nanoparticles. The dielectric study was carried out in the frequency range of 1 KHz to 4000 KHz and temperature ranging 30 °C to 350 °C using the impedance analyser. The dielectric constant decreases with increasing frequency and increases with doping ion concentration. The dielectric loss of the sample increases with increasing temperature. The anomalies in the value of dielectric constant with temperature variation are due to the presence of Ni<sup>2+</sup> ions in the sample. The magnetic and dielectric properties of the synthesized nanoparticles make them potential material for microwave absorption application.

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# Optimization of magnetic nanoparticles modifications for biomedical applications

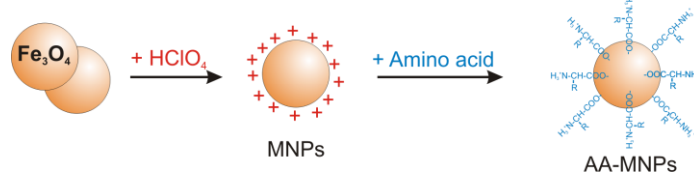
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## Abstract

Amino acid modified magnetic nanoparticles (AA-MNPs) seem to be a good candidate for conjugation of a drug effective against different diseases. That is why we focused on the preparation and characterization of several systems of MNPs modified with different biocompatible amino acids. The modification of MNPs with biocompatible amino acids of different molecular weights like glycine, D,L-lysine, tryptophan and proline was carried out by mixing an aqueous solution of AA with stabilized MNPs in different AA/MNPs input weight ratios (w/w) ranging from 0 to 30. The procedure for the preparation of MNPs and coating with amino acid is shown in the figure and described in the paper [1].



Quantification of MNPs surface coating as well as estimation of the optimum input AA/MNPs weight ratios were determined from different measurements, i.e. from measurements of the zeta potential, UV/Vis spectroscopy and thermogravimetric analysis. To find out the optimal input ratio for individual AA-MNPs systems, the adsorption efficiency was calculated as a ratio of the actual adsorbed amount of AA to theoretical loading of AA amount expressed in %. The results obtained using different methods were relatively in good coincidence. Then the optimized formulations were chosen for the next experiments. It can be concluded that the amount of AA adsorbed on surface of MNPs has tendency to decrease with increasing molecular weight of the amino acid. However, the adsorbed amount of amino acids is influenced not only by their molecular weight, but also by their chemical structure (numbers of functional groups, presence of aromatic ring or heterocycle). Such modified and optimized nanoparticles seem to be a promising candidate for *in vitro* and *in vivo* experiments and for the conjugation of commercially available corticosteroids (e.g. dexamethasone, hydrocortisone) and viral spike protein (S-protein), which could lead to the development of a biomodel for monitoring complications associated with COVID-19.

## Acknowledgments

This work is the result of the project implementation ITMS2014+ 313011AVG3 and 313011T548 supported by the Operational Programme Integrated Infrastructure funded by the ERDF.

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# **Functionalized magnetic nanoparticles for MRI imaging of drug distribution in the lungs in experimental acute respiratory distress syndrome**

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## **Abstract**

The COVID-19 era reminds us how difficult it is to treat patients with acute respiratory distress syndrome (ARDS) [1]. That's why monitoring of the spatial distribution of the directly administrated drug to the lungs is very demanded.

In this work, we focus on the synthesis, amino functionalization of magnetic nanoparticles (MNPs), conjugation of N-acetylcysteine to magnetic nanoparticles and the study of drug distribution in the lungs in the aforementioned ARDS by magnetic resonance imaging (MRI). N-acetylcysteine (ACC) was selected as a mucolytic drug commonly used in the treatment of the respiratory tract. Nanoparticle functionalization and drug conjugation were optimized and studied by different physicochemical methods such as SEM and TEM microscopy, Dynamic Light Scattering (DLS), Electrophoretic Light Scattering, UV/VIS, or magnetic measurements to obtain information about morphology, size distribution, surface charge, drug and magnetite concentrations and, last but not least, information about magnetic properties. The prepared conjugate with the optimal ACC loading concentration of 1.2 mg/ml corresponding to ACC/MNPs w/w ratio = 5 was chosen to study drug distribution in the lungs using MRI.

Amino functionalized MNPs were characterized by MRI relaxometry to determine MRI relaxation properties *in vitro* and simultaneously to reveal the spatial distribution of MNPs in the lungs *ex vivo*. We found prevailing T2 relaxation with high transverse relaxivity values ( $r_2 = 509.14 \pm 15.27 \text{ mM}^{-1}\text{s}^{-1}$ ,  $r_2^* = 663.58 \pm 19.91 \text{ mM}^{-1}\text{s}^{-1}$ ), which allowed contrast imaging and spatial distribution determination of MNPs in lungs *ex vivo*.

## **Acknowledgments**

The work was supported by the Slovak Science Grant Agency VEGA - Project No. 2/0049/23 and by the Operational Programme Integrated Infrastructure, project "BIOVID-19", ITMS 313011AVG3 co-funded by ERDF

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## Anticancer activity of betulinic acid conjugated magnetic nanoparticles

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Magnetic nanoparticles (MNPs) render a wide range of applications in many areas due to their unique properties. One of the most important uses in the field of medical applications is cancer treatment. MNPs can be used as a vehicle for magnetic drug targeting. The importance of targeted drug delivery and targeted drug therapy is to transport a drug directly to the centre of the disease under various conditions and thereby treat it deliberately, without affecting the rest of the body. For this purpose, stable magnetic fluid with low toxicity to normal cells and with ability to destroy cancer cells was designed and prepared. As a drug, betulinic acid (BA) was chosen for its undoubtedly great benefit in treating various diseases. Betulinic acid has antiretroviral, antimalarial, anti-inflammatory properties and exhibits a potent antitumor activity. It was found that betulinic acid is a selective inhibitor of human melanoma and is active in vitro against malignant brain tumours, in human leukemia, and malignant head and neck squamous cell carcinoma [1].

Iron oxide MNPs ( $\text{Fe}_3\text{O}_4$ ) were prepared by co-precipitation method, being subsequently coated with oleic acid to avoid their aggregation. To improve the biocompatibility of coated MNPs, their surface was modified by bovine serum albumin. Core diameter of MNPs in the sample of this magnetic fluid (MF) determined by magnetic measurements and by transmission electron microscopy was in the range from 4 to 11 nm. Hydrodynamic diameter mean value measured by dynamic light scattering method was ca 95 nm. Morphology of the studied magnetic particles observed by scanning electron microscopy confirmed roughly spherical shape of nanoparticles. The cytotoxicity of pure BA and a conjugate consisted of MF with betulinic acid (BA-MF) was assessed on several types of normal and cancer cell lines by MTT test. The BA-MF conjugate showed lower toxicity to normal cells than betulinic acid alone. Comparatively, BA-MF showed a much higher anticancer activity against most of tested cancer cell lines than betulinic acid alone. Very good efficacy was observed against following human cancer cell lines: cervical cells (HeLa), colorectal adenocarcinoma cells (HT29), and promyelocytic leukemia cells (HL60). On the other hand, very low efficacy of BA-MF against human liver hepatocellular cells (HepG2) was found. Betulinic acid conjugated magnetic nanoparticles are more effective than the betulinic acid itself probably due to the synergistic anticancer effect which could potentially increase the efficiency of cancer treatment.

### Acknowledgments

This work is the result of the project implementation ITMS2014+ 313011AVG3 supported by the Operational Programme Integrated Infrastructure funded by the ERDF.

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# X-Ray studies of AC dynamics in ferromagnetic ferrofluids

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Suspensions of barium hexaferrite nanoparticles (BaHF) in an isotropic solvent show spontaneous orientational and ferromagnetic order above a certain threshold concentration [1,2]. Below such threshold concentration suspensions are isotropic, while above it, nematic ordering is accompanied by spontaneous ferromagnetic ordering, leading to the formation of textbook magnetic domain structures [3]. Here, we study via SAXS the evolution of orientational correlations for a series of samples with different concentrations when subjected to oscillating magnetic fields of different amplitudes and frequencies. It is shown that the application of low frequency AC field induces nematic ordering of the nanoplatelets for isotropic suspensions. In the ferromagnetic nematic dense suspensions, while at low frequencies, the system follows the oscillations of the applied field, at high frequencies, it enters into a regime in which orientational correlations are perpendicular to the applied magnetic field. This occurs in the frequency and field amplitude range in which flow induced by magnetic field has been observed optically.

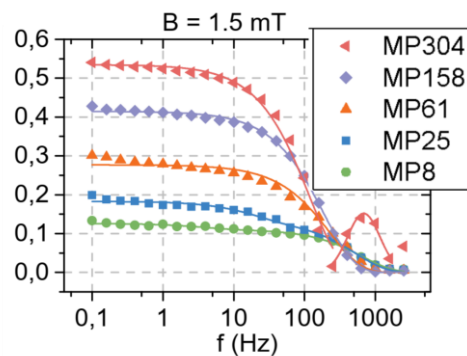


Fig.1. Frequency dependence of measured order parameter  $S$  for an external 1.5 mT field for samples of different concentrations.

## Acknowledgments

The authors acknowledge the financial support from the Slovenian Research Agency (P1-0192, P2-0089, J1-2459, PR-08973, PR-08415, PR-09494).

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## Flow-induced ferrofluid magnetization

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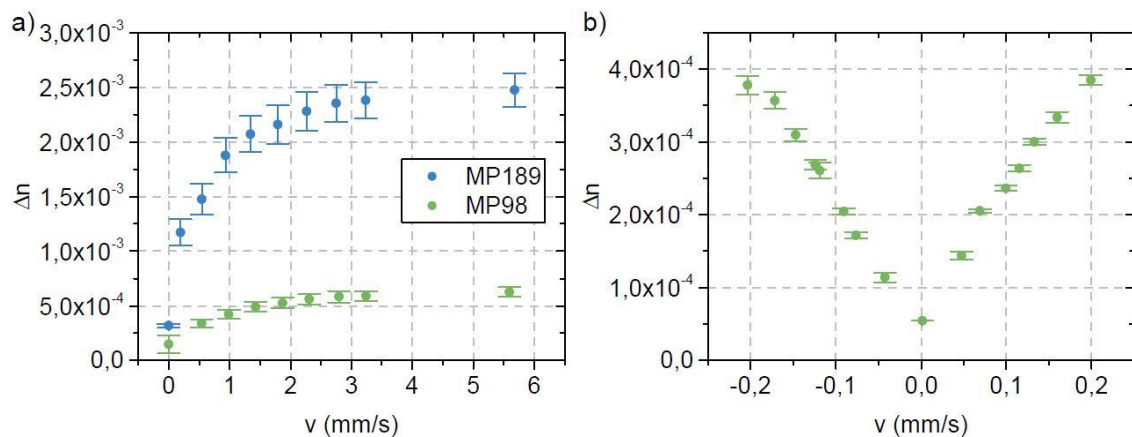
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Ferrofluids, despite their name, are not macroscopically ferromagnetic but rather paramagnetic – in the absence of magnetic field, there is no remnant magnetization. We experimentally demonstrate that fluid flow can induce macroscopic magnetization in a ferrofluid.

We filled a microcapillary with a low-concentration suspension of barium hexaferrite magnetic nanoplates in an isotropic solvent [1]. Such a suspension is isotropic, showing no orientational and ferromagnetic order in the absence of an external field. Applying a pressure gradient to the suspension gives rise to the fluid flow, which partially orients the nanoplates, resulting in a macroscopic magnetization. The effect is quantified indirectly by measuring the suspension's optical birefringence and directly by measuring the flow-induced magnetic field outside the microcapillary.



a) Measured birefringence of the ferrofluid as a function of flow velocity (shown for two different magnetic particle concentrations, 98 g/L and 189 g/L). b) An additional set of measurements for small velocities for the lower concentration sample (98 g/L).

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## Small-angle scattering investigations of ferrofluids with anisometric nanoparticles

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In the last decade, extensive studies in the field of development of various approaches to the synthesis of magnetic nanoparticles (MNPs) have been continuing. Different synthetic methods are used and under developing to obtain MNPs of desired size, morphology, stability, and biocompatibility. Many of the chemical and physical properties associated to nanoparticles are strongly dependent on the nanoparticle size, morphology, stability, etc. Recently, the production of controlled shape ferrite nanoparticles has become another requirement for researchers, and it has already been found that the size and shape of MNP control and are highly dependent on the type of surfactant and solvents used in different reaction conditions.

An important role of neutrons in the study of the structural properties of ferrofluids is well known.

Using small-angle neutron and X-ray scattering performed on the YuMO instrument of the IBR-2 reactor, RIGAKU (MPhTI) and XEUSS 3.0 stations (FLNP), respectively, XRD at Empyrean X-ray diffractometer (PANalytical), ferrofluids with anisometric nanoparticles BaFe<sub>12</sub>O<sub>19</sub> and CuFe<sub>3</sub>O<sub>4</sub>, which are important for the development of magneto-optical applications, are being investigated.

The joint studies of SANS and SAXS, as well as the use of various solvents (H<sub>2</sub>O and D<sub>2</sub>O), made it possible to obtain new information about the analyzed systems both in terms of the shape and size of nanoparticles and in terms of the distribution of surfactants on their surfaces [1, 2], very important for chemists to understand processes and develop preparation techniques.

### Acknowledgments

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# Long-Term Measurements of the Magnetization of Suspensions of Isolated Bacterial Magnetosomes

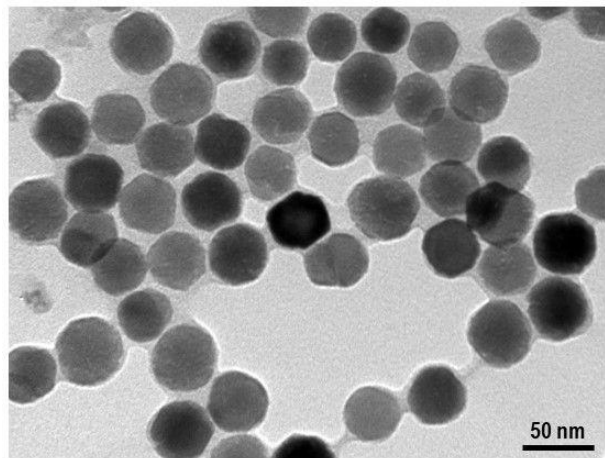
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Magnetosomes (see figure at r.h.s.) are magnetic nanoparticles biosynthesized by magnetotactic bacteria. Due to a genetically strictly controlled biomineralization process, the ensuing magnetosomes have been envisioned as agents for biomedical and clinical applications. In previous work, we examined different stability parameters of magnetosomes isolated from *Magnetospirillum gryphiswaldense* upon storage in suspension (HEPES buffer, 4°C, nitrogen atmosphere) for one year in the absence of antibiotics [1]. The



particle size distribution, the integrity of the surrounding magnetosome membrane, the colloidal stability, and the biocompatibility turned out to be not severely affected by long-term storage. However, when comparing the saturation magnetization of the freshly prepared particle suspension, and that aged by one year, a decay to one third of the initial value was found [1]. To elucidate the aging process, we are measuring since beginning of November 2022 each day four magnetization curves utilizing a vibration sample magnetometer [2], and the study is continuing. The resulting magnetization curves are fitted by means of “graphical granulometry” [3], which allows to monitor the evolution of the magnetic dipole moments, the particle number, and the saturation magnetization.

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# Synthesis, local structure and magnetic properties of core-shell $Zn_xCo_yCu_zFe_2O_4@γ-Fe_2O_3$ nanoparticles of ferrofluids

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Spinel ferrite nanoparticles are versatile materials that can be used in a wide range of areas. Aiming magnetohyperthermia applications, we present here the study of ferrofluids based on nanoparticles of mixed ferrite of cobalt, zinc, and copper, elaborated to finely tune magnetization and magnetic anisotropy of ferrite magnetic nanoparticles by varying the chemical composition. Indeed, such mixed ferrite nanoparticles could present enhanced magnetic properties for this purpose [1]. These NPs are obtained by hydrothermal coprecipitation in alkaline medium followed by a surface treatment that creates an iron-rich surface layer allowing their dispersions in acid medium [2]. The nanoparticle chemical composition has been determined by chemical analysis using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Energy Dispersive X-Ray Fluorescence Spectroscopy (EDX). This crossed analysis allows us to precisely determine the proportions of core and shell volumes and the stoichiometry of the core materials in all samples investigated here. The crystalline structure and the nanoparticle sizes were studied by using X-Ray Diffraction (XRD). Transmission Electron Microscopy (TEM) pictures show their morphology and allow a mean size determination, which well matches the one deduced from XRD analysis. An extensive magnetic characterization was carried out using a SQUID magnetometer. Low and high field (7 T) DC magnetization experiments as a function of the temperature were combined with hysteresis loop measurements to investigate the magnetic behavior of the samples. The dependence of the high field magnetization on temperature is explained within Bloch's law. From the blocking properties and the thermal dependence of the coercivity we extract the anisotropy constant for all investigated samples. The first results show that magnetization and anisotropy can be tuned by the core composition and the core/shell architecture. Additionally, the Specific Absorption Rate (SAR) has been initially measured in few samples showing rather high values when compared to the literature and the value increases with the addition of Zn and Co in the core composition.

## Acknowledgments

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# Experimental Investigation of Anisotropic Magnetic Property of Magnetic Nano-rod Dispersion Fluid

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It is well known that the clustering structure in magnetic fluid causes interesting features such as anisotropy and time-series change. Such an anisotropic change in physical property in magnetic fluid are attracted attention, and many researchers investigated the details [1]. Although inner magnetic particles in magnetic fluid are generally spherical in shape, if rod-shape magnetic particles are dispersed in magnetic fluid, such a fluid is expected to enhance anisotropic features by applying magnetic field. In this study, we investigated the anisotropic magnetic property caused by orientation of inner particles of magnetic nano-rod dispersion fluid. As a magnetic property, magnetization dynamics is reported in this abstract. The test fluids are spherical magnetic nano-particles dispersion fluid (MNP fluid) and magnetic nano-rod dispersion fluid (MNR fluid). These test fluids are prepared by ourselves. The spherical magnetic nano-particles is produced by Iolitec GmbH, but the nano-rods were synthesized by the one-pot synthesis method referred in ref. [2] by ourselves. The synthesized nano-rods have approximately 20 nm of diameter and 250 nm of length as shown in Fig.1. Magnetization dynamics of the test fluids are measured by Vibrating-Sample Magnetometer (VSM). The test sample for VSM was made by curing the test fluid by epoxy resin. In this state, there are no particle orientation in the test samples, and we marked as “No-mag.” To investigate the effect of the orientation of inner particles, magnetic field is applied to the test samples while epoxy resin of the test sample cures[3]. Fig. 2 shows magnetization curve for MNP (no mag) and MNR (no mag). As mentioned above, there are no particle orientation in these test samples. The vertical axis is normalized magnetization by the maximum saturated magnetization. This figure clearly indicates that there are no hysteresis loops in MNP (no mag), whereas hysteresis appeared and small coercive magnetic force is generated in MNR (no mag) although there is no orientation of the inner nano-rods in this case. Other results and the detailed discussion will be presented in the conference.

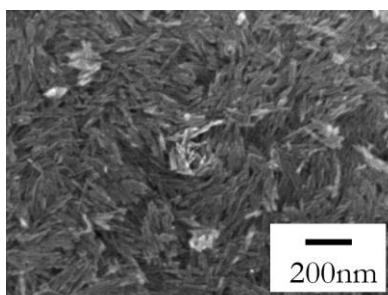


Fig. 1 SEM images of nanorod.

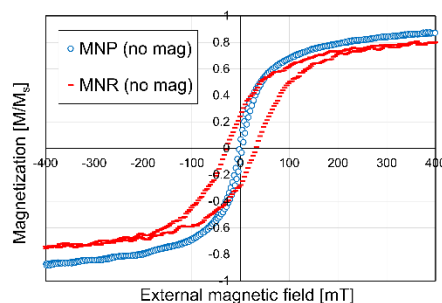


Fig.2 Magnetization dynamics.

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# POSTER SESSION 2

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Rheology and Structures



# Friction Contribution in Nanomagnetic Particle Substituted Magnetorheological Fluid

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The dynamic rheology (oscillation mode) of MR fluid with varying nanoparticle concentrations has shown that cohesive energy (i.e., between particle-particle) was reduced by increasing the concentration of nanoparticles [1]. The observed behaviour was attributed to the decrease in particle-particle friction. Nanoparticles fill the surface roughness of micron size particles and reduce friction. The main contribution of this article is to evaluate friction's role in an anisotropic MR fluid in the flow mode using the model, equation 1.

$$\tau = \tau_{sy} \left[ 1 \pm \frac{\left\{ 1 - \exp\left(-\frac{\dot{\gamma}}{\dot{\gamma}_c}\right) \right\}}{\left(1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_c}\right)^a\right)} \right] + K\dot{\gamma}^n \quad (1)$$

Here,  $K$  is the consistency term,  $\dot{\gamma}_c$  and  $a$  are the critical shear rate and exponent, respectively. The  $n$  is a fit parameter. Here  $\tau$  is the stress and  $\tau_{sy}$  is the static yield stress. The first term in Eq. (1) is the modified yield stress, and the second term is viscous contribution. The sign  $\pm$  depends on when the flow starts, and it is a function of friction and magnetic field strength.

## Results & discussion

The flow curves were analysed with the aid of the model, Eq (1). Fig.(a) shows the influence of particle weight fraction on the stress properties at 28.6 kA/m. The sign changes from + to -, (in equation 1) indicating the contribution of friction in MR fluid without nanoparticles.

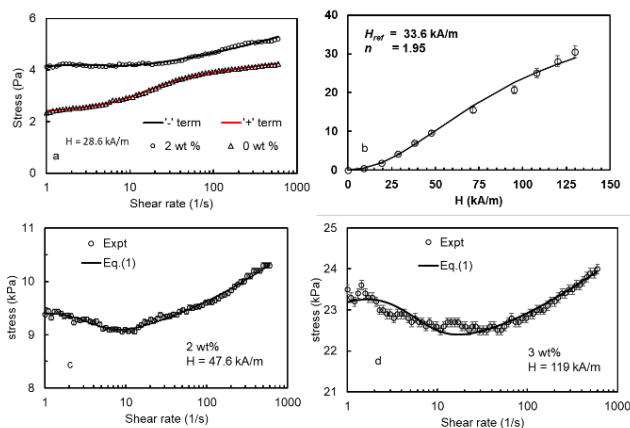


Fig. b shows the variation of yield stress with magnetic field. Figs. (c) and (d) are for two different concentrations; the field stress curves show the fit with the model at small shear rates. The relative viscosity variance of friction contribution was also confirmed by mason number variation.

## Acknowledgements

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technology for the research.

1. Mujiba et al., *Rheologica Acta* volume 59, pages 887–904 (2020)

# Influence of nanoparticles morphology in magnetorheological fluids

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## Abstract

In this work the effect of solid phase shape in magnetorheological fluids properties was studied. For this purpose, magnetite ( $\text{Fe}_3\text{O}_4$ ) spherical, octahedral, truncated octahedral and rod-like nanoparticles-based MR suspensions were prepared. The more faceted nanoparticles (octahedral and truncated octahedral) were synthesized through the thermal decomposition of iron(III) oleate in a mixture of octadecene and benzyl ether, which produced highly crystalline magnetic nanoparticles. On the other hand, the rod-like particles were synthesized using the solvothermal method. A mixture of oleic acid, hexadecylamine, iron(0) pentacarbonyl and 1-octanol was heated inside a Teflon-lined autoclave for 6 h at 200 °C resulting in the formation of  $\text{Fe}_3\text{O}_4$  rod-shape nanoparticles. Finally, the spherical nanoparticles employed were commercial and were supplied by Sigma-Aldrich.

The prepared MR fluids were composed of the corresponding shape  $\text{Fe}_3\text{O}_4$  nanoparticles, mineral oil and additives to improve the particles dispersion and stability. The particles concentration was varied between 5% vol and 15 %vol for each case. The impact of the particle shape and concentration on MR fluid properties was measured through magnetic and rheological characterizations of the suspensions under the influence of different magnetic field intensities. The capability of each suspension to recover its initial rheological properties after being exposed to a magnetic field was also measured. Finally, the contribution of magnetostatic and hydrodynamic forces acting on MR fluid over other forces was measured through Mason number. In accordance with other studies [1] good qualitative agreement was observed between the MR suspensions yield stress and the magnetization measurements. Moreover, regardless of morphology and concentration, the MR fluids analyzed in this study saturate at the same magnetic field intensity.

## Acknowledgments

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# Magnetorheological properties of oil-in-oil magnetic Pickering emulsions

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Magnetic nanoparticles affect the rheological properties of magnetic fluids and Pickering emulsions, especially in the magnetic field. A Pickering emulsion is an emulsion stabilized by solid particles accumulated at the surface of droplets. Magnetic Pickering emulsion can be utilized in the biomedical and industry field due to its unique magnetic properties, which can be controlled under an external magnetic field. In this research, we investigated the magnetorheological effect for rarely tested oil-in-oil Pickering emulsions and compared them with the simpler and better-characterized oil-based magnetic fluids and emulsions without stabilizing particles.

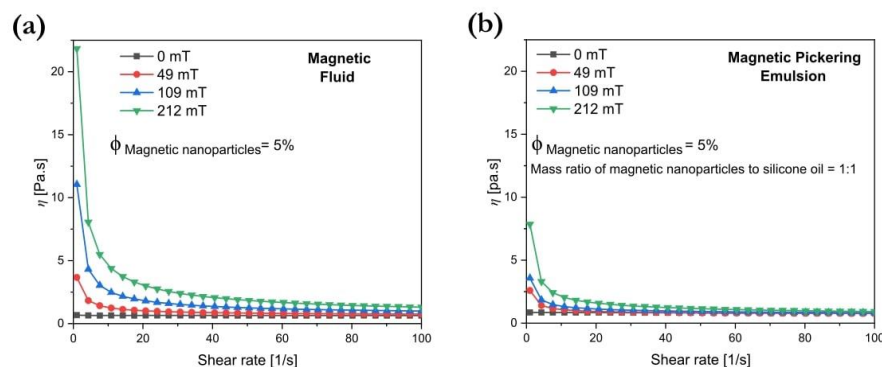


Figure 1. The viscosity in the function of shear rate for different DC magnetic fields for (a) oil-based magnetic fluid and (b) magnetic Pickering emulsion.

The experimental results show that oil-in-oil magnetic Pickering emulsion exhibits magnetoviscous effect similar to magnetic fluid as shown in Figure 1. Due to different internal structural changes, the increase of viscosity in the function of magnetic field intensities is lower in magnetic Pickering emulsion despite the same mass fraction of the magnetic nanoparticles in the system.

## Acknowledgments

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# High magnetization composite magnetic fluid: magnetorheology and application in rotating seals

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The sealing capacity of magnetofluidic (MF) rotating seals is limited by the highest magnetization of the sealing ferrofluids (FFs) used of about 1000-1200 G. A sharp, almost an order of magnitude increase of the supported pressure drop is possible by using magnetorheological (MR) suspension as sealing fluid, due to the much higher saturation magnetization of MR fluids compared to FFs [1]. However, rotating seals with MR fluids have several shortcomings, such as a significant increase of the friction torque due to the growth of the shear stress in the strong magnetic field specific to MF seals and, also, the possible sedimentation of micron size multi-domain iron particles and leakage of the carrier liquid. At least partly, the mentioned issues can be avoided by using ferrofluid based extremely bidisperse MR suspensions of micrometer size iron (Fe) particles dispersed in a ferrofluid [2] as sealing fluid [3]. The present work refers to a bidisperse suspension of several tens (about 65) nm size Fe nanoparticles in a ferrofluid carrier having 500 G saturation magnetization, a composite magnetizable fluid with improved kinetic stability. The volume concentration of iron NPs varies from 5 to 15% in the ferrofluid carrier and produce significant changes of the flow properties in magnetic field of the suspension, from Newtonian to a strongly non-Newtonian behavior. The evaluation of the magnetic and magnetorheological behavior includes the dependence of magnetization, viscosity curves, magnetoviscous effect and dynamic yield stress on the volume fraction of the Fe nanoparticles dispersed in the ferrofluid carrier. The increased sealing capacity of the composite fluids in comparison with the ferrofluid carrier was experimentally investigated in case of a rotating MF feedthrough.

## Acknowledgments

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# Anisotropic Thermophysical Properties of MR Fluids Prepared by Using Selective Adsorption Function

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Conventional MR fluids have the problem of particles settling due to their large size and density. Recently, a new ultra-stable dispersion MR fluid has been developed by adding the selective adsorption function in the MR fluid [1]. This stable dispersion of  $\mu\text{m}$ -sized particles enables long-time stability of anisotropies such as viscosity and thermal conductivity. In the present study, anisotropies of viscosity and thermal conductivity of the stable MR fluids in the presence of a magnetic field were examined using a magnetorheometer (MRD, Anton Paar) and homemade magnetic field-imposed type transient hot wire method, respectively. Additionally, utilizing the selective adsorption function,  $\mu\text{m}$ -sized copper particles are added and stably dispersed to the MRF in order to achieve more improvement in thermodynamic properties. As a result, the MRF dispersing copper particles increases thermal conductivity by at least about 14% when the homogeneous magnetic field is applied parallel to the temperature gradient. The MR effect was investigated, changing the plate gap of the magnetorheometer. The shear stress – shear rate shows a unique behavior: the shear stress decreases and then increases with the shear rate increasing at the gap between the plates set to be 0.4 mm.

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# Effect of surface roughness on the rheological behaviour of MR fluids

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The behaviour of MR fluids in contact with various surface finishes is an important issue for applications where stress transmission at the fluid-solid interface determines the operating conditions of the system, as well as for applications where MR fluids are used for the abrasive magnetorheological finishing. The first applies mainly to conventional applications, i.e. magnetorheological clutches, dampers, brakes, etc. In the second case, poor interaction between fluid particles and the workpiece can result in insufficient microcutting force and, consequently, too little or no machining efficiency. Some studies on the effect of surface roughness on rheological measurements of MR fluids indicate that an increase in roughness can result in an increase in measured stresses [1 - 4].

This study presents the results of an analysis of the influence of selected factors on the behaviour of MR fluid in contact with surfaces of different roughness coefficients. The study included measurements on a rotational rheometer with increased roughness of the measuring surfaces. The change in surface roughness was shown to have a significant effect on the shear and normal stress values. An increase in surface roughness can result in a significant reduction in the stress transfer capacity of interfacial contact. An explanation for the observed phenomena has been proposed.

## Acknowledgements

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# POSTER SESSION 2

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Synthesis





## **Magnetite mineralization inside cross-linked protein crystals**

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Crystallization in confined spaces is a widespread process in nature that also has important implications for the stability and durability of many man-made materials. It has been reported that the confinement can alter essential crystallization events, such as nucleation and growth, and thus, having an impact on crystal size, polymorphism, morphology and stability. Therefore, the study of nucleation in confined spaces can help us understand similar events that occur in nature, such as biomineralization, and expand our knowledge in the field of crystallography. Besides its intrinsic interest, basic models at laboratory scale are scarce due to the difficulty to obtain well-defined confined spaces that allow a simultaneous study of the mineralization process outside and inside the cavities. Herein, we have studied magnetite precipitation in the channels of cross-linked protein crystals (CLPCs) with different channel pore size, as a model of crystallization in confined spaces. Our results show that nucleation of an Fe-rich phase occurs inside the protein channels in all cases, but, by a combination of chemical and physical effects, channel diameter of CLPCs exerted a precise control in the size and stability of those Fe-rich nanoparticles. The small diameters of protein channels restrain the growth of metastable intermediates to around 2 nm and stabilize them over time. At larger pore diameters, recrystallization of the Fe-rich precursors into the more stable phases was allowed. This study highlights the impact that crystallization in confined spaces can have in the physicochemical properties of the resulting crystals and shows that CLPCs can be interesting substrates to study this process.

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## Shape comparison of magnetite nanoparticles and their gold coating for dual therapy

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In this work we study the behaviour of three types of magnetite nanoparticles with different size and geometry under the action of an alternating magnetic field and laser irradiation. Both techniques consist of raising the temperature of a localized area by means of these nanoparticles to induce tumour death, known as magnetic hyperthermia and photothermia [1,2].

For this purpose, two types of nanorods (namely NR1, and NR2) are synthesized, being the average lengths of  $550 \pm 90$  nm (aspect ratio 1:5) and  $40 \pm 15$  nm (1:8) respectively. Furthermore, they will be compared with nanospheres (S) of diameter  $60 \pm 9$  nm (Fig.1). In addition, as a bio-application is sought, these particles will be coated with a polymeric (PEI) layer that will make them biocompatible. In the case of the nanospheres, the coating will be done "in situ" [3], while for the nanorods a previously described technique can be applied [4].

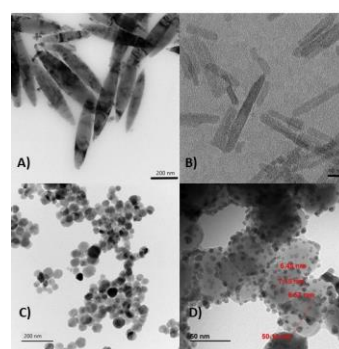


Fig. 2 HRTEM images of magnetite nanoparticles NR1 (A), NR2 (B), S (C) and gold-coated S (D).

For this reason, we chose nanospheres for the creation of gold/magnetite nanostructures with the aim of improving known therapies: taking advantage of the good optical properties of gold, we intend to increase its performance as a photothermal agent. Finally, the synergy between both stimuli is studied by irradiating while subjecting the sample to an alternating magnetic field. The results obtained show that it is possible to obtain a higher temperature increase, and therefore, it is possible to decrease the field parameters and irradiation power, achieving a less harmful therapy.

### Acknowledgments

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## **Fabrication, characterization and bioactive properties of poly-L-lysine and chitosan functionalized magnetic nanoparticles**

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Designing magnetic nanoparticles (MNPs) has been in the focus of scientific interest for the last decades. The using of iron oxide nanoparticles in various biomedical applications requires functionalization of their surface to be biocompatible. A wide spectrum of coating compounds was suggested for surface modification.

In our work we have prepared, characterized and studied the biological activity of magnetic nanoparticles with negatively charged silica-layer as an initial coating (SiO<sub>2</sub>@MNPs). These SiO<sub>2</sub>@MNPs were subsequently functionalized with biocompatible biomacromolecules poly-L-lysine (PLL) and chitosan (Chit).

The properties of SiO<sub>2</sub>@MNPs, PLL-SiO<sub>2</sub>@MNPs and Chit-SiO<sub>2</sub>@MNPs were studied by different methods. The formation of the PLL and Chit layers on the surface of SiO<sub>2</sub>@MNPs was confirmed by FTIR spectroscopy. Different thermal behavior of the chitosan and poly-L-lysine in the physical mixtures and the PLL-SiO<sub>2</sub>@MNPs and Chit-SiO<sub>2</sub>@MNPs also indicates that poly-L-lysine and chitosan were bounded on the SiO<sub>2</sub>@MNPs. The high positive values of zeta potential indicate that the PLL and Chit-coated nanoparticles are positively charged due to the cationic characteristics of poly-L-lysine and chitosan. The fact that isoelectric point of SiO<sub>2</sub>@MNPs shifts by some pH units when the particles are functionalized with PLL and Chit is in favor of the adsorption of organic molecules by magnetic nanoparticles. The TEM images show that nanoparticles were roughly spherical in shape. Magnetization measurements confirmed superparamagnetic behavior of all samples and at the same time indicate that the coating processes do not affect the intrinsic magnetic properties of the particles. We have also found that SiO<sub>2</sub>@MNPs, PLL-SiO<sub>2</sub>@MNPs and Chit-SiO<sub>2</sub>@MNPs bind RNA with different efficiency.

The presented data strongly suggest that coating of the magnetic nanoparticles affects their physico-chemical properties as well as their biological activity.

### **Acknowledgments**

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## Design, preparation and radiolabeling of amino functionalized magnetic nanoparticles for potential theranostic use

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Amino modified (proline, tryptophan and poly-L-lysine) magnetic nanoparticles were used to design potential theranostic agents for cancer diagnosis and for combined radionuclide and hyperthermia therapy [1]. Detailed characterization of prepared MNPs was performed using of various techniques, such as dynamic light scattering, electron microscopy, magnetization measurements or thermogravimetric analysis. Measurements in an alternating and non-alternating magnetic field were also conducted. For the first time amino acid-functionalized magnetic nanoparticles were labeled with theranostic radionuclides <sup>131</sup>I and <sup>177</sup>Lu. Radiolabeling with <sup>131</sup>I did not provide agents with sufficient radiochemical purity and stability. On the other hand, direct radiolabeling with <sup>177</sup>Lu at room and elevated temperature provided satisfactory results in case of proline and tryptophan modified MNPs. Poly-L-lysine functionalized MNPs obtained by radiolabeling at 80 °C reached very high radiochemical purity and high *in vitro* and *in vivo* stability. Moreover, SAR value obtained for poly-L-lysine functionalized MNPs shows their high potential for the possible hyperthermia application. Biodistribution of radiolabeled functionalized MNPs was studied in healthy male Wistar rats. The results are encouraging for the future research on discovering the full potential of <sup>177</sup>Lu-PLL-MNPs (80 °C) for hyperthermia-based cancer treatment in combination with radioactivity.

### Acknowledgments

The work was supported by the Operational Programme Integrated Infrastructure, project “BIOVID-19”, ITMS 313011AVG3 co-funded by ERDF.

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## Influence of coating on peroxidase-like activity of magnetic nanoparticles

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Today, nanoscale materials are of great scientific and technical interest in a wide range of fields. Magnetic nanoparticles (MNPs), which are characterized by low toxicity, superparamagnetic properties, biocompatibility, biological degradation, and the ability to be excreted from the body naturally, take their place among many nanoscale materials. Therefore, MNPs are receiving considerable attention in biological applications such as magnetic resonance imaging (MRI), magnetic hyperthermia, and targeted drug delivery. In addition, it was reported that MNPs have an intrinsic peroxidase-like activity, which makes it possible to use them as a tool for detecting and visualizing tumor tissue. Moreover, MNPs have almost unchanged catalytic activity in a wide range of temperature and pH and are also significantly more stable compared to natural enzymes peroxidases [1]. However, the influence of the concentration of the stabilizing material on the peroxidase-like activity of MNPs has been rarely reported. In this work, we prepared MNPs by the coprecipitation method followed by their coating with chitosan (a bioactive polymer) to obtain stable chitosan-modified magnetic nanoparticles (Chit-MNPs). The comprehensive physicochemical characterization of uncoated MNPs and Chit-MNPs was carried out to determine their structure, morphology, and magnetic properties. The peroxidase-like activity of uncoated MNPs and Chit-MNPs was also investigated by oxidation of the chromogenic substrate N,N-diethyl-p-phenylenediamine sulfate (DPD) with hydrogen peroxide. Uncoated MNPs and Chit-MNPs were found to be able to activate H<sub>2</sub>O<sub>2</sub> and oxidize DPD to a purple product with an absorption maximum at 550 nm. Under optimized conditions, the absorbance of the product responded linearly to H<sub>2</sub>O<sub>2</sub> concentration in the range from 6.53 to 97.53 mM for both samples. Furthermore, when increasing the concentration of imposed chitosan on the surface of magnetic nanoparticles (for the lowest H<sub>2</sub>O<sub>2</sub> concentration of 6.53 mM), linear decrease in catalytic activity was detected, i.e. even small amount of bound chitosan on MNPs reduces peroxidase-like activity of MNPs. This result could be useful for new potential applications, especially in biomedicine and cellular biology, for example, visualizations of pathological tissues during MRI, cell labelling, cell separation etc.

### Acknowledgments

The work was supported by the Operational Programme Integrated Infrastructure, project “BIOVID-19”, ITMS 313011AVG3 co-funded by ERDF.

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# Mms7-mediated biomimetic magnetic nanoparticles

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The increasing use of magnetic nanoparticles (MNPs) and the problems that have been identified for chemically produced (and commercial) ones (e.g., poor magnetic and/or surface properties, the need for coating to provide functional groups with the subsequent shield of their magnetic core) demand new efficient and eco-friendly production processes that generate magnetic nanoparticles with improved properties. One of the most novel strategies for the synthesis of MNPs mimics the biomineralization process carried out by magnetotactic bacteria to synthesize the magnetite crystals of their magnetosomes. This synthesis is mediated by magnetosome-associated proteins such as MamC, Mms6 or Mms7, which bind iron and control crystal growth [1]. MamC (*Magnetococcus marinus* MC-1) has been successfully used in the synthesis of biomimetic magnetic nanoparticles (BMNPs), obtaining larger nanoparticles with better magnetic and surface properties than inorganic MNPs [2]. However, the effect of other proteins such as Mms7 on crystal growth is not well studied. Thus, in this work, Mms7 protein from *M. marinus* MC-1 was purified and used to synthesize BMNPs following the biomimetic mineralization protocol employed with MamC [2]. The properties of the resulting Mms7-mediated BMNPs were compared with the MamC-mediated ones. Transmission electron microscopy images show that Mms7-mediated BMNPs have distinct shapes and a similar size to the MamC-mediated BMNPs (~40 nm). Fourier-transform infrared spectroscopy and X-ray diffraction analysis indicate that the nanoparticles are composed of magnetite and contain Mms7, at least attached and probably embedded. The isoelectric point of these nanoparticles is ~4.7, they are usually less aggregated than the MamC-mediated BMNPs, and they can increase their temperature in photothermia and magnetic hyperthermia experiments. Finally, they are capable of binding molecules such as PL48 (anticancer drug), can be internalized in liver cells and are cytocompatible, these characteristics being very useful for a possible application of these nanoparticles as drug carriers for targeted chemotherapies.

## **Acknowledgments**

This work was supported by the project PDC2021-121135-100 from the Ministry of Science and Innovation (Spain).

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# The phase-director effect of iron glycinate complexes in fast microwave-assisted synthesis of iron oxide nanoparticles

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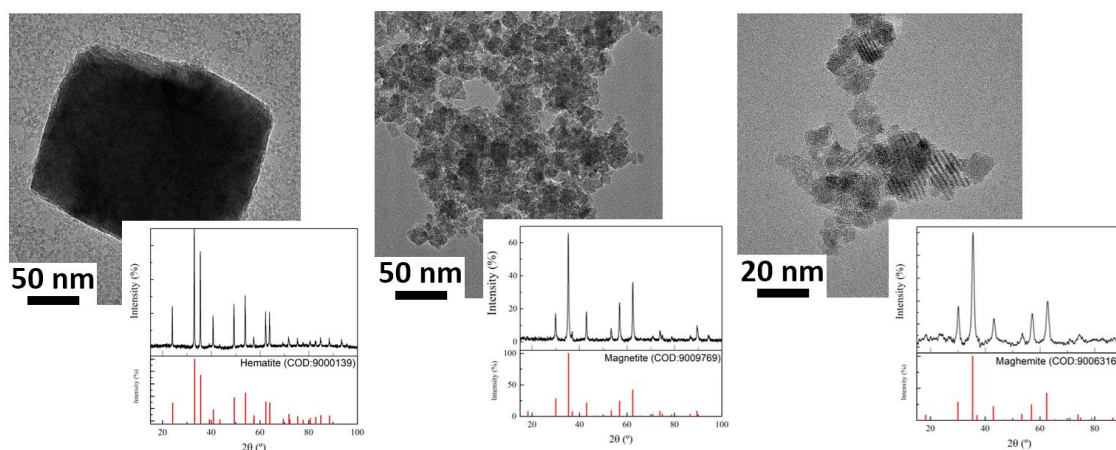
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The production of magnetic nanoparticles for use in humans is subjected to stringent requirements by the regulatory authorities as part of their approval process. The relevant parameters and conditions to the synthesis are known – especially for iron oxides –, but parasitic phases appear at times even in reactions that are carried out using the most popular methods [1]. This entails additional post-production separation and purification steps, with the subsequent increase in economic and time costs.

Following an aqueous microwave synthesis method of iron oxide nanoparticles, we have found that we can avoid the formation of parasitic phases within the same reaction through the use of glycine. We hypothesise that the fast formation iron glycinates prevents the appearance of unwanted iron aquo-complexes or oxohydroxides, also allowing a homogeneous size distribution in the resulting nanoparticles. This is particularly useful to avoid premature reactions that take place while precursors are mixed. Glycine also serves as a surfactant, limiting the growth of unwanted clusters and favouring the formation of nanoparticles of a few nanometres in size, leading to stable colloids.



**Figure 1.** TEM pictures of the synthesized hematite (left), maghemite (right) and magnetite (centre) nanoparticles by the proposed glycine-based microwave method.

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# Synthesis and Characterization of Multi-Responsive CoFe<sub>2</sub>O<sub>4</sub>@Au@Polymer Hybrid Materials

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To enhance the properties of magnetic fluids, or more specifically the magnetic nanoparticles (MNPs) that make up those fluids, multiple groups investigated methods to synthesize a composite NP system consisting of a superparamagnetic core such as magnetite NPs and a gold shell.<sup>[1]</sup> The addition of the gold shell adds the plasmonic properties and catalytic activity of the nanostructured gold to the magnetic fluid and additionally increases the stability of MNPs against dissolution and oxidation. These “magnetic gold particles” can be localized in a specific area by magnetic fields and thus improve the application for example in biomedicine compared to ordinary gold NPs, which undergo heavy diffusion within the system.<sup>[2]</sup> The abovementioned properties make the MNP@Au-NPs an interesting alternative to ordinary MNPs or gold NPs and also open up different applications utilizing the properties of both components.<sup>[2]</sup> The functionalization with different ligands is an integral part of optimizing any nanostructure for a specific application. The choice of the ligands controls colloidal stability in the medium, can enable biocompatibility, or introduce specific properties like stimuli-responsiveness to the particle system. Furthermore, the ligands in the system can be used to integrate the colloidal particle system into a material like a gel or a film. Polymers are an example of a ligand class, which can be used to stabilize the colloid, add responsiveness to the system and finally work as a platform to turn a colloidal suspension into a smart hybrid material. Using controlled radical polymerization, polymers with specific architectures, chain lengths and functionalization degrees can be tailored to support the particle system for a specific application.<sup>[3]</sup> In our work, the concept of a multi-responsive hybrid material based on a CoFe<sub>2</sub>O<sub>4</sub>@Au particle system inside of a responsive polymer matrix is demonstrated. The synthesis of the particle system was achieved by the seeded growth of gold on the surface of CoFe<sub>2</sub>O<sub>4</sub>-NPs in an aqueous medium. The CoFe<sub>2</sub>O<sub>4</sub>@Au-NPs were then embedded into the polymer matrix by the functionalization of the gold surface with the thermo-responsive, multi-functional polymer chains. The finally obtained hybrid material was characterized regarding its magnetic, plasmonic and thermo-responsive properties and compared to these of the components that make up the hybrid material. Concluding the investigation, it was shown that the hybrid material exhibits magnetic behavior, plasmonic properties as well as the thermo-responsive properties of the polymer matrix. That suggests that the described synthesis route can be used to create multi-responsive CoFe<sub>2</sub>O<sub>4</sub>@Au@Polymer hybrid materials using a wide range of polymers with different molecular structures, chain lengths and responsive properties.

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# **Synthesis of protein (albumin) microbubbles endorsed with iron oxide nanocrystals for magnetic manipulation and heat delivery**

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Since magnetic nanoparticles when exposed to an alternating magnetic field can generate heat, they are great candidates for applications in which thermal energy is essential to accomplish the anticipated experimental purpose. In nanomedicine, this phenomenon is used for localized cancer therapy (magnetic hyperthermia), complementing or being a promising alternative to chemotherapy and radiotherapy. [1][2][3] For achieving better biocompatibility and gaining additional features, the magnetic nanoparticles must be functionalised by different coatings or immersed in hybrid systems. With this in mind, albumin protein microbubbles obtained by sonochemistry method were chosen to attain a hybrid system, which hosts iron oxide nanoparticles (two samples with different size and shape) in the protein shell, and become endorsed with magnetic properties for manipulation and/or heat delivery applications. [4][5]

## **Acknowledgments**

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# Synthesis and characterization of supramolecular peptide-based magnetic hydrogels

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## Abstract

Short peptides are an example of hydrogelators which can form supramolecular structures as a consequence of specific and local interactions of molecules themselves. These molecules undergo self-association usually forming hierarchical structures at the nanoscale or at the macroscale [1]. Among many hydrogelators, N-(9-Fluorenylmethoxycarbonyl)-L-phenylalanine (Fmoc-FF) is one of the most frequently used.

In this study, iron nanoparticles have been modified to get hydroxyl and amine groups onto their surface. It was shown that the final properties of supramolecular magnetic hydrogels can be affected by the interactions between functionalized nanoparticles and hydrogelator molecules. DFT calculation clearly showed that attractive interactions between carbonyl group of the Fmoc-FF and protonated amine group may result in structural rearrangement of Fmoc-FF molecule.



Fig. 1. Formula of Fmoc-FF molecule (left), resulting magnetic hydrogel (center), micrograph of the hydrogel structure by ESEM microscopy; the scale bar is 2 μm (right)

Those interactions and resulting rearrangements are linked with the structural and mechanical properties of the final magnetic hydrogels, while keeping their biocompatibility unchanged, when compared to non-magnetic Fmoc-FF-based hydrogel. The collected results show the important role of the surface layer of nanoparticles dispersed in the hydrogel in governing the macroscopic properties.

## Acknowledgments

This research was funded by Polish National Science Centre, grant number 2021/41/B/ST5/03490, titled “*Hierarchically cross-linked hydrogels: theoretical and experimental design for biomedical applications*”.

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# Release of diclofenac sodium from non-magnetic and magnetic alginate hydrogels

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## Abstract

Biomedical applications of hydrogels have constantly been evolving during the last years, driven by discoveries in the field of biology and chemistry. Compared with other types of biomaterials, hydrogels have increased biocompatibility, tunable biodegradability, and tunable porous structure and thus permeability. These advantageous materials are finding increasing application in many biomedical fields, including drug delivery, tissue engineering, 3D printing and biosensing and actuating applications [1].

Hydrogel delivery systems can leverage therapeutically beneficial outcomes of drug delivery as they can provide spatial and temporal control over the release of various therapeutic agents, including small-molecule pharmaceuticals. Serving as platforms in which various physiochemical interactions with the encapsulated drugs control their release [2].

In this work, the controlled release of diclofenac sodium (used here as a model nonsteroidal anti-inflammatory drug) from alginate-based hydrogels was studied. Alginate hydrogels were additionally doped with magnetic nanoparticles according the known procedure [3] to assess the impact of the presence and absence of the external magnetic field on the release profiles of diclofenac sodium from the obtained hydrogels. The obtained results indicate that the release profiles of diclofenac sodium depend on many factors, including the cross-linking degree of alginate hydrogels, but also on the presence of magnetic nanoparticles.

## Acknowledgments

This research was funded by Polish National Science Centre, grant number 2021/41/B/ST5/03490, titled “*Hierarchically cross-linked hydrogels: theoretical and experimental design for biomedical application?*”.

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# POSTER SESSION 2

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Theory and Computer simulations



# Flexible magnetic filaments in an applied field

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It is known that ferromagnetic filaments buckle in response to the inversion of the magnetic field [1]. The existing numerical algorithms for their simulation are using the so-called projection operator technique to account for the inextensibility of the filament [1]. Here we are describing algorithm where inextensibility is satisfied directly without using the projection operator [2] which allows us to account for the inertia of filament and consider the oscillations of the filament at subcritical values of the magnetoelastic number. The set of nonlinear PDE in 2D case reads

$$\frac{\partial x}{\partial l} = \cos\vartheta; \frac{\partial y}{\partial l} = \sin\vartheta; A \frac{\partial^2 \vartheta}{\partial l^2} = \sin\vartheta F_x - \cos\vartheta F_y - MH \sin\vartheta; \rho_l \frac{\partial^2 x,y}{\partial t^2} = \frac{\partial F_{x,y}}{\partial l} \quad (1)$$

at boundary conditions for free and unclamped ends  $\frac{\partial \vartheta}{\partial l} \Big|_{0,L} = 0; F_{x,y} \Big|_{0,L} = 0$ . In the case of small deformations ( $\vartheta \ll 1$  scaling the length with the length of filament  $L$ , time with  $\left(\frac{A}{\rho_l L^4}\right)^{-1/2}$  the dimensionless set of equations for small perturbations reads ( $Cm = \frac{MHL^2}{A}$ )

$$\frac{\partial y}{\partial l} = \vartheta; \frac{\partial^2 \vartheta}{\partial l^2} = -F_y - Cm\vartheta; \frac{\partial^2 y}{\partial t^2} = \frac{\partial F_y}{\partial l} \quad \text{at boundary conditions}$$

$$\frac{\partial^2 y}{\partial l^2} \Big|_{0,1} = 0; \left(\frac{\partial^3 y}{\partial l^3} + Cm \frac{\partial y}{\partial l}\right) \Big|_{0,1} = 0. \quad (2)$$

As a result the eigenfrequencies of filament oscillations  $\omega$  are found as eigenvalues of the problem  $\frac{d^4 y}{dl^4} + Cm \frac{d^2 y}{dl^2} - \omega^2 y = 0$  at boundary conditions (2). Stable oscillations are possible for the first even mode  $y = A_1 \text{ch}(\alpha_1(l - 0.5)) + A_2 \cos(\alpha_2(l - 0.5))$ ,

where  $\alpha_1 = \sqrt{\frac{\sqrt{Cm^2 + 4\omega^2} - Cm}{2}}$ ;  $\alpha_2 = \sqrt{\frac{\sqrt{Cm^2 + 4\omega^2} + Cm}{2}}$  and  $\omega$  is found as solution of

$$(\alpha_1 \alpha_2^2 - \alpha_1 Cm) \sin\left(\frac{\alpha_2}{2}\right) + (\alpha_2 \alpha_1^2 + \alpha_2 Cm) \cos\left(\frac{\alpha_2}{2}\right) \text{th}\left(\frac{\alpha_1}{2}\right) = 0 \quad (3)$$

Real  $\omega \neq 0$  solutions of Eq.(3) exist at  $0 < Cm < \pi^2$  and are shown in Fig. 1. Points are results of numerical solution of Eqs.(1) for the case of small amplitude perturbations and are in good agreement with analytical results. The algorithm described is used to simulate the dynamics of a filament under the action of viscous friction and its self-propulsion in AC fields.

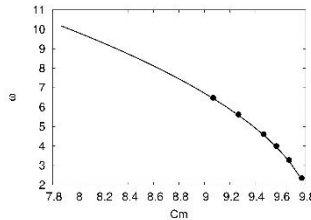


Fig. Eigenfrequencies of rod in subcritical region. Points numerical calculation by (1).

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# Simulating magnetization dynamics in suspensions of magnetic filaments with super-paramagnetic colloids.

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Incorporating magnetic nanoparticles within permanently cross-linked structures, opens the possibility for synthesis of highly magneto-responsive systems, with improved optical, thermal, mechanical, rheological, and surface-adsorption properties compared to conventional magnetic fluids. Magnetic filaments (MFs) are polymer-like chains of magnetic, nano-sized colloids, and are an example of the aforementioned complex systems that are a promising platform for engineering novel, magnetically controlled filtering and flow control elements in micro-fluidic devices, just to give an example.[1,2] Understanding the interplay between anisotropic, dipolar interactions and filament architecture is crucial to be able to tune the macroscopic response of MFs.

In this contribution we study a suspension of magnetic filaments and show that considering nonlinear contributions to the magnetization of super-paramagnetic colloids, is essential to capture the magneto-mechanical response of MFs in bulk, consisting of magnetizable colloids. Furthermore, we contrast the results obtained using the Langevin magnetization law with nonlinear contributions approach to our state-of-the-art, hybrid approach, using a kinetic-Monte-Carlo scheme in which magnetic colloids are represented as Stoner-Wohlfarth particles. With this approach we can simulate temperature sensitive magnetization dynamics of superparamagnetic or ferromagnetic NPs in soft matter systems on long time scales, capturing internal magnetization dynamics, including both Brownian and Néel relaxation mechanisms. We report on the equilibrium properties of filaments in bulk, and their mechanical and magnetic response to static and time dependent magnetic fields. While on the level of a single filament, magneto-mechanical properties are in general more dependent on the crosslinking approach than on the magnetic nature of colloids, in bulk, the long-range nature of dipolar interactions in quasi-infinite systems underlines the necessity of a sophisticated model of magnetic colloids that can be magnetized by the presence of magnetic and dipole fields.

## **Acknowledgments**

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# Full micromagnetic simulations of rotating magnetic nanoparticles for hyperthermia

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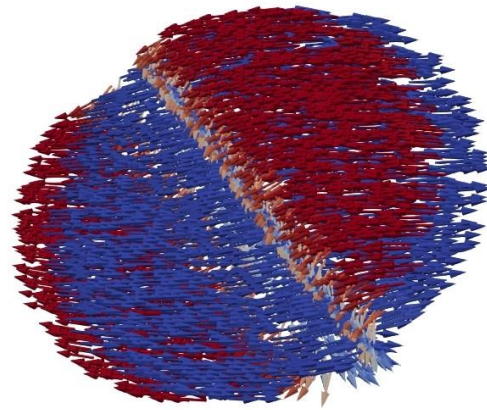
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## Abstract

To further our understanding of the relaxation processes of a magnetic nanoparticle and to find a way to better harness those processes for magnetic hyperthermia, we simulated a system with coupled micromagnetics and mechanical dynamics [1]. The magnetic dynamics are solved for multiple micromagnetic spins via the finite difference method while also solving for the rotation of the particle in parallel leading to a self-consistent solution of the coupled problem. This approach improves the accuracy and level of detail of the simulations. Compared to the macro-spin model the dynamics differ significantly, especially for particles with sizes at or above the single-domain limit.

The talk will discuss results of the macro-spin simulations and the full micromagnetic simulations of uniaxial magnetic nanoparticles subjected to an alternating magnetic field and suspended in a viscous fluid. The micromagnetic simulations show a more complex steady state behavior of the particles that leads to a reduction in energy losses due to a weaker magnetic torque on the easy axis. Examples of the rotation of spins in single-domain particles and the propagation of domain walls in anti-ferromagnetic disks (see figure) and their effect on the rotation of the particle will also be shown.



## Acknowledgments

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# Magnetic response of magnetic nanogels

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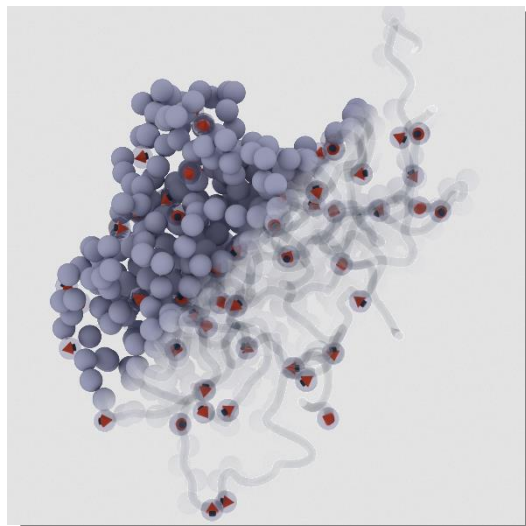
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Hydrogels are soft materials that have attracted solid interest over the last six decades and are widely used in chemical, biomedical, and even civil engineering applications. Today, at the forefront of the gels' realm, stand out nanogels, often additionally functionalized, for instance, by magnetic nanoparticles - so-called magnetic nanogels (MNGs) (see Fig. below).

Understanding the dynamics and internal structure of MNGs is crucial for their applications, for example, in targeted drug delivery. Based on the experimentally obtained dynamic magnetic susceptibility ( $\chi$ ) of the system [1], we developed a numerical model of MNG [2], which was further used in molecular dynamics (MD) simulations in conjunction with the Lattice-Boltzmann (LB) scheme to describe how the MNG internal structure manifests itself in magnetic and rheological properties on the suspension scale.

We study in detail how  $\chi$  is affected by the distribution of crosslinkers: uniform, with a Gaussian distribution from the center to the periphery, and reverse. How  $\chi$  depends on MNGs concentration. Finally, we analyze the case of mixed response when an external magnetic field and hydrodynamic shear flow are simultaneously applied to the suspension of MNGs.



Coarse-grained bead-spring model of an MNG

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# **A Three-Dimensional Software Library for the Simulation of Multiphase Ferrohydrodynamic Flows**

Jacob Maarek,<sup>1</sup> Phillip Yecko,<sup>2</sup> David Trubatch<sup>3</sup> .

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We present a three dimensional multiphysics computational fluid dynamics framework for the direct numerical simulation of magnetic fluid flow. We augment an existing multiphase DNS code, calculating the magnetic field in the domain and then computing the magnetophoretic force from the applied field. We consider different formulations for the magnetic body force density derived from the magnetic stress tensor. These formulations are compared with a series of validation cases including droplet deformation in an applied uniform field, multiple droplet interaction in an applied field, and the surface normal instability. Lastly we simulate a toy problem representative of a ferrofluid sessile drop in the presence of a solenoid. The ferrohydrodynamic code presented can be used to gain insight in the complex coupled dynamics present in such flows and perform simulated experiments for applications research.

# Self-Assembly of Colloidal Magnetic Platelets

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A series of advances in synthesis techniques have fuelled the study of ferrofluids wherein the colloidal nanoparticles have either magnetic anisotropy or shape anisotropy. These have both been shown to strongly affect the macroscopic properties of ferrofluids.

This contribution focuses on a specific combination of the two aforementioned factors, which combines aspects of colloidal liquid crystal and magnetic soft matter research; a ferrofluid of colloidal magnetic nanoplatelets with dipole moments oriented perpendicular to the platelets' plane. It has been shown that this suspension exhibit a macroscopic ferromagnetic nematic phase. Using Langevin Dynamics simulations, we study the microstructure of the suspension to understand how the cluster formation differs from suspensions of dipolar hard spheres, and calculate the magnetic susceptibilities. We also present binary mixtures of platelets with different strengths of the magnetic dipole moment.

Comparing simulation findings to known theories and available experimental results, we show the limitations of a single-dipole approximation, as well as how strongly the shape anisotropy affects various self-assembly scenarios.

# Experimental and numerical investigation on magnetic self-assembled microstructures

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## Abstract

In the present study, the magnetic field induced self-assembly processes of magnetic microparticles dispersed in aqueous liquids are experimentally and numerically investigated. The magnetic microparticles are formed into the chain-like microstructures when applying an external magnetic field. Then, the length of these self-assembled chain-like microstructures are measured on a microfluidic chip which is manufactured based on Polydimethylsiloxane (PDMS). Further, a three-dimensional numerical model based on lattice Boltzmann method (LBM) and immersed boundary method (IBM) is developed to simulate the self-assembly process of magnetic microparticles in a microchannel. The chain-like microstructures under different magnetic intensities are calculated, and their distribution and the average length are investigated. The coincident results of the experiments and numerical simulations provide a guidance on non-contact manipulate the magnetic materials to form the chain-like structures by magnetic field.

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