



NON TOXIC AND MEDICINAL APPLICATIONS OF FERROFLUIDS

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ABSTRACT

Ferrofluids—suspensions of magnetic nanoparticles—exhibit as a specific feature the magnetic control of their physical parameters and of flows appearing in such fluids. This magnetic control can be achieved by means of moderate magnetic fields with a strength of the order of 10 mT. This sort of magnetic control also enables the design of a wide variety of technical applications such as the use of the magnetic forces for basic research in fluid dynamics. The overall field of ferrofluid research is already about 40 years old. Starting with the first patent on the synthesis of magnetic nanoparticle suspensions by S Papell in 1964, a vivid field of research activities has been established. Looking at the long time in which ferrofluids have been the focus of scientific interest, one can ask the question, what kind of recent developments justify a special issue of a scientific journal?

New developments in a field, which depends strongly on a certain material class and which opens research possibilities in different scientific fields will nowadays usually require an interdisciplinary approach. This kind of approach starting from the synthesis of magnetic suspensions, including research concerning their basic properties and flow behaviour and focusing on new applications has been the core of a special research programme funded by the Deutsche Forschungsgemeinschaft (DFG) over the past 6 years. Within this programme—entitled ‘Colloidal Magnetic Fluids: Basics, Synthesis and Applications of New Ferrofluids’—more than 30 different research groups have been coordinated to achieve new results in various fields related to ferrofluid research.

The basic approach of the program has been the assumption that new applications well beyond the typical ferrofluid techniques, for example loud speaker cooling or sealing of rotary shafts, will require tailored magnetic suspensions with properties clearly focused towards the need of the application. While such tailoring of fluids to certain well defined properties sounds like a straightforward approach one has to face the fact that it requires a clear definition of the required properties. This definition itself has to be based on a fundamental physical knowledge of the processes determining certain magnetically controlled phenomena in ferrofluids. To make this point concrete one can look into the detailed aims of the mentioned research program. The application areas identified for the future development of research and application of suspensions of magnetic nanoparticles have been on the one hand the biomedical application—especially with respect to cancer treatment—and on the other hand the use of magnetically controlled rheological properties of ferrofluids for new active technical devices.

keywords : Ferrofluids, Superparamagnets, Magnetorheological Fluid, Energy arvesting, Optics.

Ferrofluids are colloidal liquids made of nanoscale ferromagnetic, or ferrimagnetic, particles suspended in a carrier fluid (usually an organic solvent or water). Each tiny particle is thoroughly coated with a surfactant to inhibit clumping. Large ferromagnetic particles can be ripped out of the homogeneous colloidal mixture, forming a separate clump of magnetic dust when exposed to strong magnetic fields. The magnetic attraction of nanoparticles is weak enough that the surfactant's Van der Waals force is sufficient to prevent magnetic clumping or agglomeration. Ferrofluids usually^[3] do not retain magnetization in the absence of an externally applied field and thus are often classified as "superparamagnets" rather than ferromagnets.

The difference between ferrofluids and magnetorheological fluids (MR fluids) is the size of the particles. The particles in a ferrofluid primarily consist of nanoparticles which are suspended by Brownian motion and generally will not settle under normal conditions. MR fluid particles primarily consist of micrometre-scale particles which are too heavy for Brownian motion to keep them suspended, and thus will settle over time because of the inherent density difference between the particle and its carrier fluid. These two fluids have very different applications as a result.

Ferrofluids are composed of nanoscale particles (diameter usually 10 nanometers or less) of magnetite, hematite or some other compound containing iron, and a liquid. This is small enough for thermal agitation to disperse them evenly within a carrier fluid, and for them to contribute to the overall magnetic response of the fluid. This is similar to the way that the ions in an aqueous paramagnetic salt solution (such as an aqueous solution of copper(II) sulfate or manganese(II) chloride) make the solution paramagnetic. The composition of a typical ferrofluid is about 5% magnetic solids, 10% surfactant and 85% carrier, by volume.

Particles in ferrofluids are dispersed in a liquid, often using a surfactant, and thus ferrofluids are colloidal suspensions – materials with properties of more than one state of matter. In this case, the two states of matter are the solid metal and liquid it is in. This ability to change phases with the application of a magnetic field allows them to be used as seals, lubricants, and may open up further applications in future nanoelectromechanical systems.

True ferrofluids are stable. This means that the solid particles do not agglomerate or phase separate even in extremely strong magnetic fields. However, the surfactant tends to break down over time (a few years), and eventually the nano-particles will agglomerate, and they will separate out and no longer contribute to the fluid's magnetic response.

The term magnetorheological fluid (MRF) refers to liquids similar to ferrofluids (FF) that solidify in the presence of a magnetic field. Magnetorheological fluids have micrometre scale magnetic particles that are one to three orders of magnitude larger than those of ferrofluids.

However, ferrofluids lose their magnetic properties at sufficiently high temperatures, known as the Curie temperature.



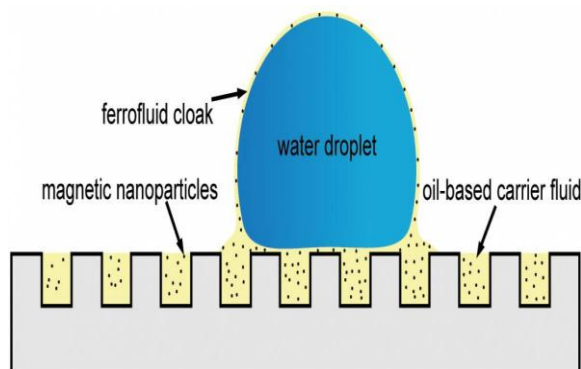
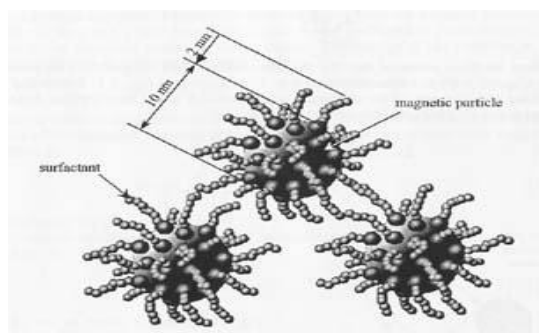
II. FERROFLUID SURFACTANTS

The surfactants used to coat the nanoparticles include, but are not limited to:

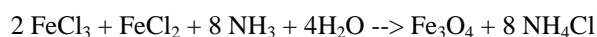
- oleic acid
- tetramethylammonium hydroxide
- citric acid
- soy lecithin

These surfactants prevent the nanoparticles from clumping together, ensuring that the particles do not form aggregates that become too heavy to be held in suspension by Brownian motion. The magnetic particles in an ideal ferrofluid do not settle out, even when exposed to a strong magnetic, or gravitational field. A surfactant has a polar head and non-polar tail (or vice versa), one of which adsorbs to a nanoparticle, while the non-polar tail (or polar head) sticks out into the carrier medium, forming an inverse or regular micelle, respectively, around the particle. Electrostatic repulsion then prevents agglomeration of the particles.

While surfactants are useful in prolonging the settling rate in ferrofluids, they also prove detrimental to the fluid's magnetic properties (specifically, the fluid's magnetic saturation). The addition of surfactants (or any other foreign particles) decreases the packing density of the ferroparticles while in its activated state, thus decreasing the fluid's on-state viscosity, resulting in a "softer" activated fluid. While the on-state viscosity (the "hardness" of the activated fluid) is less of a concern for some ferrofluid applications, it is a primary fluid property for the majority of their commercial and industrial applications and therefore a compromise must be met when considering on-state viscosity versus the settling rate of a ferrofluid. A ferrofluid in a magnetic field showing normal-field instability caused by a neodymium magnet beneath the dish Preparation of Ferrofluids:



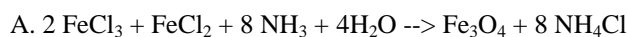
Ferrofluids containing magnetite can be prepared by combining the appropriate amounts of an Fe(II) salt and an Fe(III) salt in basic solution, a combination that causes the mixed valence oxide, Fe_3O_4 , to precipitate from solution:



However, the particles of magnetite must remain small in order to remain suspended in the liquid medium. To keep them small, magnetic and van der Waals interactions must be overcome to prevent the particles from agglomerating. Thermal motion of magnetite particles smaller than ~10 nm in diameter is sufficient to prevent agglomeration due to magnetic interactions.

The van der Waals attraction between two particles is strongest when the particles approach each other at close distances. Therefore, one method of preventing agglomeration due to van der Waals and magnetic forces is to keep the particles well separated. This separation can be accomplished by adding a surfactant to the liquid

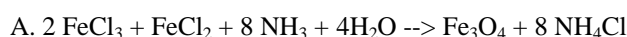
medium. The surfactants can generate either steric or electrostatic repulsions between the magnetic particles. For example, *cis*-oleic acid can be used for oil-based ferrofluids as a surfactant that produces steric repulsions. The surfactant is a long-chain hydrocarbon with a polar head that is attracted to the surface of the magnetite particle; thus a surfactant coating is formed on the surface. The long chains of the tails act as a repellent cushion and prevent the close approach of other magnetite particles (Figure 1).



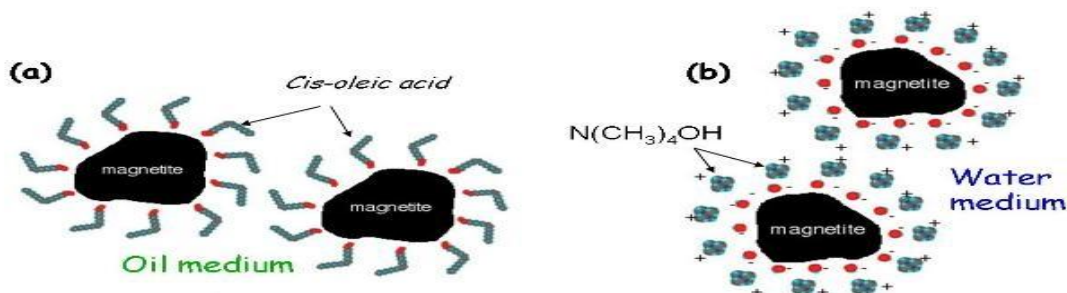
B. Add *cis*-oleic acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$, in oil.

C. Remove water:

Ionic surfactants such as tetramethylammonium hydroxide can be used as a surfactant that produces electrostatic repulsion in an aqueous medium. The hydroxide ions are attracted to the surface of each magnetite particle, forming a negatively charged layer at the magnetite surface. The tetramethyl ammonium cations are attracted to the negatively charged layer, forming a positive layer. When magnetite particles approach each other the repulsions between their positively-charged layers keeps them from getting too close. (Figure 2).



B. Replace excess NH_4OH on Fe_3O_4 surface with $\text{N}(\text{CH}_3)_4\text{OH}$



Source: University of Wisconsin MRSEC

Figure 1. A preparation of ferrofluids: (A) the synthetic conditions for production of $\text{Fe}_3\text{O}_4(s)$; and (B) addition of surfactant to give small particle of Fe_3O_4 (shaded circles) stabilized by interaction of the hydroxide anions with the magnetite and by the interactions of the tetramethylammonium cations with the water serving as the medium.

Some ferrofluids are so attracted to magnetic fields that they will stand up along magnetic field lines, forming an array of spikes (Figure 3).

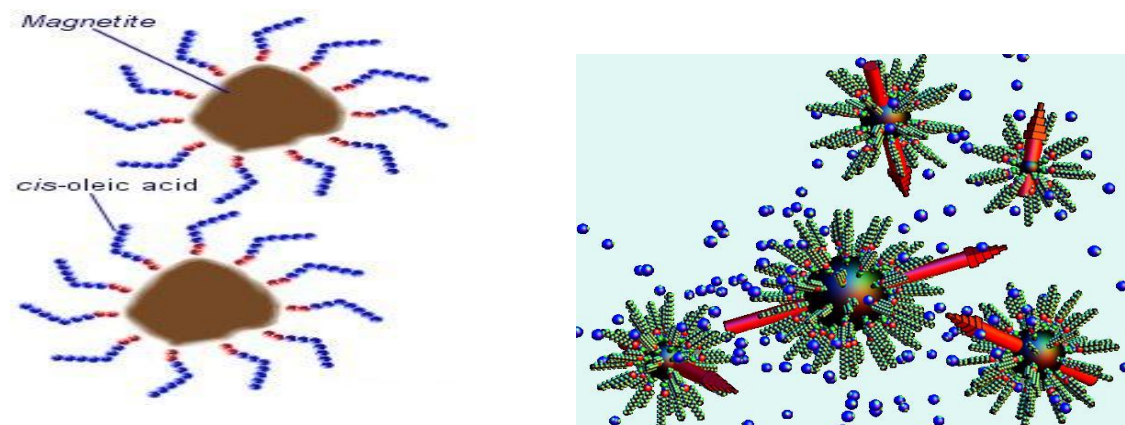


Figure 2. Top and side views of the magnetic spiking phenomenon observed when a cow magnet is placed beneath a Petri dish containing a ferrofluid. The ferrofluid aligns with the magnetic field lines of the magnet to produce the spikes.

III. APPLICATIONS

3.1 Electronic Devices

Main article: Ferrofluidic seal

Ferrofluids are used to form liquid seals around the spinning drive shafts in hard disks. The rotating shaft is surrounded by magnets. A small amount of ferrofluid, placed in the gap between the magnet and the shaft, will be held in place by its attraction to the magnet. The fluid of magnetic particles forms a barrier which prevents debris from entering the interior of the hard drive. According to engineers at Ferrotec, ferrofluid seals on rotating shafts typically withstand 3 to 4 psi; additional seals can be stacked to form assemblies capable of withstanding higher pressures.

3.2 Mechanical engineering

Ferrofluids have friction-reducing capabilities. If applied to the surface of a strong enough magnet, such as one made of neodymium, it can cause the magnet to glide across smooth surfaces with minimal resistance.

Ferrofluids can also be used in semi-active dampers in mechanical and aerospace applications. While passive dampers are generally bulkier and designed for a particular vibration source in mind, active dampers consume more power. Ferrofluid based dampers solve both of these issues and are becoming popular in the helicopter community, which has to deal with large inertial and aerodynamic vibrations.

3.3 Materials science research

Ferrofluids can be used to image magnetic domain structures on the surface of ferromagnetic materials using a technique developed by Francis Bitter.

3.4 Loudspeakers

Ferrofluids are commonly used in loudspeakers to remove heat from the voice coil, and to passively damp the movement of the cone. They reside in what would normally be the air gap around the voice coil, held in place by the speaker's magnet. Since ferrofluids are paramagnetic, they obey Curie's law and thus become less magnetic at higher temperatures. A strong magnet placed near the voice coil (which produces heat) will attract cold ferrofluid more than hot ferrofluid thus forcing the heated ferrofluid away from the electric voice coil and toward a heat sink. This is a relatively efficient cooling method which requires no additional energy input.

3.5 Medical applications

Several ferrofluids were marketed for use as contrast agents in magnetic resonance imaging, which depend on the difference in magnetic relaxation times of different tissues to provide contrast. Several agents were introduced and then withdrawn from the market, including Feridex I.V. (also known as Endorem and ferumoxides, discontinued in 2008; resovist (also known as Cliavist (2001 to 2009); Sinerem (also known as Combidex, withdrawn in 2007; Lumirem (also known as Gastromark (1996 to 2012; Clariscan (also known as PEG-fero, Feruglose, and NC100150), development of which was discontinued due to safety concerns.

3.6 Spacecraft propulsion

Ferrofluids can be made to self-assemble nanometer-scale needle-like sharp tips under the influence of a magnetic field. When they reach a critical thinness, the needles begin emitting jets that might be used in the future as a thruster mechanism to propel small satellites such as CubeSats.

3.7 Analytical instrumentation

Ferrofluids have numerous optical applications because of their refractive properties; that is, each grain, a micromagnet, reflects light. These applications include measuring specific viscosity of a liquid placed between a polarizer and an analyzer, illuminated by a helium–neon laser.

3.8 Medical applications

Ferrofluids have been proposed for magnetic drug targeting. In this process the drugs would be attached to or enclosed within a ferrofluid and could be targeted and selectively released using magnetic fields.

It has also been proposed for targeted magnetic hyperthermia to convert electromagnetic energy into heat.

It has also been proposed in a form of nanosurgery to separate one tissue from another—for example a tumor from the tissue in which it has grown.

3.9 Heat transfer

An external magnetic field imposed on a ferrofluid with varying susceptibility (e.g., because of a temperature gradient) results in a nonuniform magnetic body force, which leads to a form of heat transfer called thermomagnetic convection. This form of heat transfer can be useful when conventional convection heat transfer is inadequate; e.g., in miniature microscale devices or under reduced gravity conditions.

Ferrofluids of suitable composition can exhibit extremely large enhancement in thermal conductivity (k ; ~300% of the base fluid thermal conductivity). The large enhancement in k is due to the efficient transport of heat through percolating nanoparticle paths. Special magnetic nanofluids with tunable thermal conductivity to viscosity ratio can be used as multifunctional ‘smart materials’ that can remove heat and also arrest vibrations (damper). Such fluids may find applications in microfluidic devices and microelectromechanical systems (MEMS).

3.10 Optics

Research is under way to create an adaptive optics shape-shifting magnetic mirror from ferrofluid for Earth-based astronomical telescopes.

Optical filters are used to select different wavelengths of light. The replacement of filters is cumbersome, especially when the wavelength is changed continuously with tunable-type lasers. Optical filters tunable for different wavelengths by varying the magnetic field can be built using ferrofluid emulsion.

3.11 Energy harvesting

Ferrofluids enable an interesting opportunity to harvest vibration energy from the environment. Existing methods of harvesting low frequency (<100 Hz) vibrations require the use of solid resonant structures. With ferrofluids, energy harvester designs no longer need solid structure. One example of ferrofluid based energy harvesting is discussed in the journal article, *Electromagnetic ferrofluid-based energy harvester*. First a ferrofluid is placed inside a container that is wrapped with a coil of wire. The ferrofluid is then externally magnetized using a permanent magnet. When external vibrations cause the ferrofluid to slosh around in the



container, there is a change in magnetic flux fields with respect to the coil of wire. Through Faraday's law of electromagnetic induction, voltage is induced in the coil of wire due to change in magnetic flux.

IV. FERROFLUIDS FOR MEDICINE

Lately the health care professionals are turning to magnetic particles for different tasks arising in process of medical treatment. The exploitability of this method is obvious because magnetic particles can be controlled by external magnetic field, and no allentesis is needed.

V. FERROFLUID FOR TREATING ULCERS AND FISTULAS

The method comprises inserting ferrofluid into fistulous tract and attaching a permanent magnet to its outer opening. The fixed position of ferrofluid in fistulous tract carefully seals the fistula, not interfering with the healing process.

VI. FERROFLUID HELPS TO PRESERVE VISION

Patients with affected retina can be prevented from blindness. Retina is a very thin, photosensitive tissue n the rearer side of the eye. If it is somehow affected or starts laminating due to a trauma or sickness, vision grows weaker and a person can become blind. Usually silicone liquid is used to get the retina back to its place, but magnetized ferrolfluid can do much better.

This method is much more accurate since it allows the fluid to move under action of an external magnet and reach the areas of the eye that can't be reached by other means.

VII. COURIER FERROFLUID

Casual drug therapy is becoming more and more popular due to magnetic couriers — magnetic particles attached to biomolecules, drug or diagnostics agent particles. Magnetic couriers ensure two unique advantages for bio systems. Used for making other molecules, they can be detected by a highly sensitive magnetoresistive sensor system. On the other hand, molecules attached to magnetic couriers are easy to manipulate by external magnetic field. It is associated both with delivering medicine to a designated internal organ and with keeping it there.

VIII. FERROFLUID HYPERTHERMIA

Ferrofluid-based hyperthermia is primarily meant for treating one of the most malignant brain tumor — glioblastoma.

The concept of this technique is the following. Fluid containing microscopic iron particles is inserted into the tumor tissue under anesthesia. The iron particles are uptaken by the cancer cells. Then the tumor is acted upon by external magnetic field, and iron nanoparticles grow hotter, up to 45°C. Such a heating destroys tumor tissue and intensifies the follow-up X-ray therapy simultaneously. Ferrofluid-based hyperthermia has been in researched for 12 years and has successfully tested on animals.

IX. MAGNETIC NANOPARTICLES DESTROY CANCER CELLS

Under magnetic field, multifunctional nanoparticles can reach into cancer cells, piercing their membranes. Nanoparticle core is iron oxide. The researchers have discovered that under magnetic field, the particles inside cancer cells are able to break through the membrane of cancer cells.

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