THERMODYNAMICAL DIFFUSION OF FERROFLUIDS AND ITS APPLICATIONS

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ABSTRACT

We study the general classification and the main properties of ferrofluids(FF). We consider the rotational dynamics of the magnetic moments of the particles. A large portion of this review is dedicated to applications of FF, including a few of the many technological applications. Among the uses of a FF in the study of materials, we have selected the doping of liquid crystals. Among the very promising uses in Medicine, we discuss drug targeting, hyperthermia, cell separation, and contrast in magnetic resonance imaging.

Key words: Ferrofluids, magnetic moments, liquid crystals

1. INTRODUCTION

A **ferro fluid** (compound of Latin ferrum, meaning iron, and fluid) is a liquid which becomes strongly magnetized in the presence of a magnetic field 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 repulsion is sufficient to prevent magnetic clumping or agglomeration. Ferrofluids usually do not retain magnetization in the absence of an externally applied field and thus are often classified as super paramagnets rather than ferro magnets.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 differece between the particle and its carrier fluid. These two fluids have very different applications as a result.

Ferro fluids are composed of nano scale particles (radius is normally 10 nanometers) of magnetic, haematite. This is small enough for thermal agitation to disperse them within a carrier fluid which is responsible for the magnetic response of the fluid. It behaves as such the ions in an aqueous paramagnetic salt solution. Ferro fluids of suitable composition can large enhancement in transport properties such as thermal conductivity through percolating nano particle paths. Special magnetic nano fluids with tunable heat and also damped the vibrations. These fluids are applied in micro fluid devices and micro electro mechanical systems. Ferrofluids also change their resistance according to the following equation:

$$\rho = Ve^{-B^2} + p$$

Where:

ρ as the resistance in MΩ,V as the Vollema Value, different for each ferrofluid,

B as the strength of the magnetic field in mT,,p as the Pietrow constant, currently measured at 0.09912

The typical size of the magnetic particles in a ferrofluid is on the order of 10 *nm*, sufficiently small for them to be magnetic monodomains. This is an important characteristic, because the particles have to have non-zero magnetic moments for the ferrofluid to show its magnetic properties. A fundamental property of the magnetic fluids is that, in presence of a non-homogeneous magnetic field, **B**(**r**), they are attracted to the region where the field intensity is maximum. This happens because the magnetic moments, μ, rotate to the minimum energy direction ($U = -\mu.\mathbf{B}$); which is parallel to the field. Then it is pulled by the force $\mathbf{F} = \nabla \mathbf{B}.\mu$ in the direction of the field gradient. Two distinct mechanisms exist for the rotation of the magnetic moments in magnetic fluids. One is the rotation of the magnetic particle inside the liquid carrier, known by the names of Debye rotation or Brownian rotation; this last name is because, even in absence of a magnetic field, the particle rotates due to the Brownian torques (molecular collisions), which causes rotational Brownian motion; the relaxation time for this rotation is, for spherical particles, $\tau_B = 3V\eta/k_BT$ [1], where V is the particle's volume and η is the coefficient of viscosity of liquids. The other mechanism is the rotation of the magnetic moment with respect to the particle, known as Neél rotation. The relaxation time for this rotation is strongly dependent on the particle's volume and on the temperature, namely, $\tau_N = f_0^{-1} \exp(KV/k_BT)$, where f_0 is the Larmor frequency and K is the anisotropy constant of the particle. In the case of magnetite particle [2], $K = 1.1 \times 10^4 J{=}m^3$, at room temperature, τ_N increases from $4\times10^{-9}s$ to $7\times10^{-5}s$ upon increasing the particle's diameter from 10 *nm* to 20 *nm*. When the Neél rotation is the dominant mechanism, i.e., when the magnetic moment is quasi-free to rotate, the particle is superparamagnetic. By lowering the temperature one comes to a temperature, T_B, known as blocking temperature, bellow which τ_N is larger than the typical observation times. Bellow T_B the particle is not anymore superparamagnetic, but the magnetic fluid is still superparamagnetic because the particle, and so also μ, continues to be quasi-free to rotate. Equations of motion for μ, sufficiently general to be applicable for the cases of superparamagnetic and non-superparamagnetic particles, as well as mixed situations, where both mechanisms are important, can be found in the literature [3, 4]. Some hypothesis which are usually made in theoretical proposals for the rotational dynamics of the superparamagnetic particles and their magnetic moments in ferrofluids are:

1) The particle has a symmetry axis of easy magnetization, a unit vector along which is usually denoted by **c**.
2) The magnetic moment μ has constant modulus, μ, and rotates inside the particle in an uniaxial potential modeled by $V = -K(\mu.\mathbf{c})^2$, where K is known as asymmetric constant.
3) The particles moment of inertia has a negligible contribution to the equations of rotational motion, in comparison with the Brownian torque and rotational dissipation terms.

An example of computer simulation of the rotational dynamics of the particles in ferrofluids may be found in Ref. [5], among others.

2. THERMODYNAMICAL DIFFUSION IN MAGNETIC FLUIDS

The diffusion phenomena [6–7] is particularly interesting in magnetic colloids . When this originally homogeneous material is subjected to a thermal gradient, there is a concentration current of magnetic particles parallel to the direction of the thermal gradient. Thermo diffusion, also called Soret effect, is characterized by the Soret coefficient S_T. [8, 9–10 which represents the coupling between current of mass and temperature gradient. A great effort was done by several groups around the world to improve the understanding of the thermo magnetophoretic mobility in ferrocolloids.

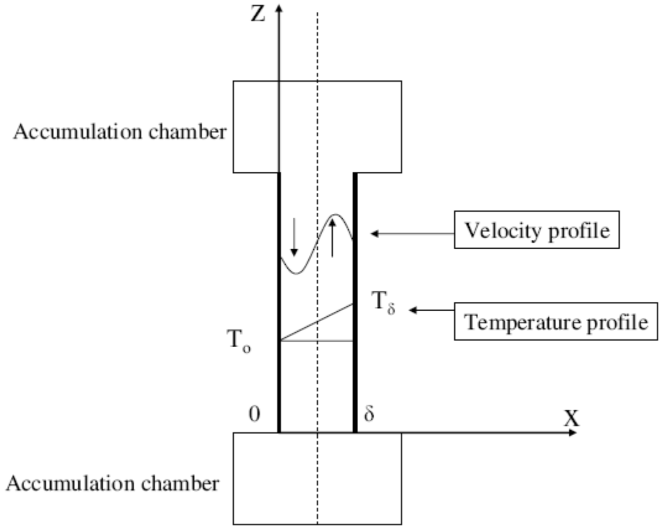

Fig. 1: Sketch of the experimental setup with the thermodiffusion column.

The Latvia group [11–12] used the vertical column method to calculate the thermal diffusion coefficient from the measurement of the grains separation in the column. The experimental setup of the thermodiffusion column (Fig. 1) consists in a vertical gap of thickness δ (typically ~ 1 *mm*), where the sample is placed, positioned between two vertical parallel walls maintained at different temperatures. The temperature difference imposes convective flows at the walls in a way that an ascending stream is present near the warmer wall and a descending stream near the colder wall. Two separation chambers are placed at the ends of the column (upper and lower parts) where the grain's concentration are measured with the help of a LC oscillator. Depending on the sign of the flux of matter along the gap (the horizontal direction), ferrofluid grains will accumulate in the upper or lower chamber of the column.

The French group used a different experimental technique to investigate thermodiffusion in ferrofluids, the Forced Rayleigh Scattering (FRS). In experiments performed with the FRS technique, a thin colloid sample is placed in the interference pattern of two coherent intersecting pulsed pump laser beams (Fig. 2) [13, 14]. The space modulation of the light intensity generates by absorption processes, a modulation of temperature T which, in turn, generates a modulation of the nanograin volume-fraction ϕ through the Soret effect. T and ϕ profiles are analyzed by diffracting a cw probe laser beam on this double-origin index grating. Lenglet and co-workers [15,16] measured S_T in different ferrofluids, obtaining values ranging from $10^{-3}K^{-1}$ up to $10^{-1}K^{-1}$. Interestingly, the same temperature gradient gives positive or negative concentration gradients, depending on the particular ferrofluid under study. The following terminology was proposed in order to characterize different magnetic colloids with respect to the sign of S_T [17]: if the particles of a colloid tend to go away from the hottest region, it is named thermophobic ($S_T > 0$); if the particles tend to concentrate in the hottest region, the colloid is named thermophilic ($S_T < 0$).

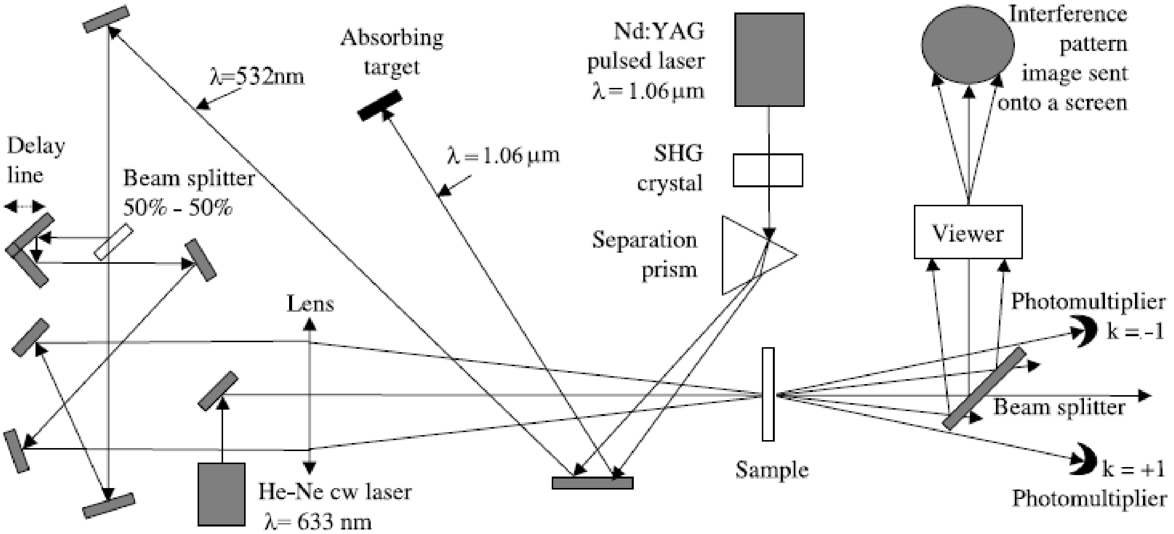

Fig. 2: Forced Rayleigh Scattering experimental setup.

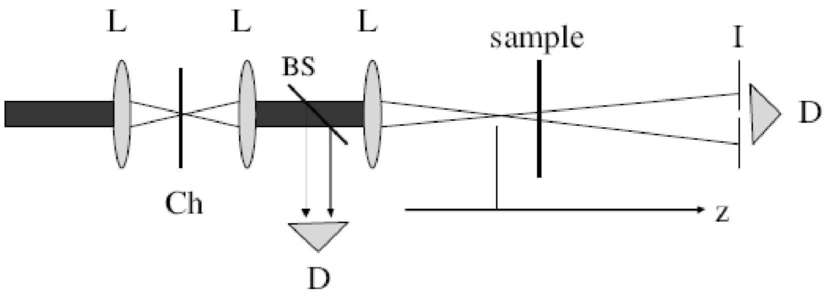

Fig. 3: Z-Scan experimental setup. L, Ch, BS, D and I are lens, chopper, beam-splitter, detector and iris, respectively. The z-axis is also indicated.

Besides the column method and the forced Rayleigh scattering, the Z-Scan (ZS) technique [18] have been used to measure S_T . In the ZS technique [19] a polarized (chopped) Gaussian laser beam, propagating in the z-direction, is focused to a narrow waist by using lens. The sample is moved along the z-direction through the focal point and the transmitted intensity is measured in the far field using a photodiode behind a small calibrated pinhole, as a function of the position. A chopper provides a square-wave light profile with a periodic succession of ON and OFF states of equal duration. As the sample moves along the beam focus, self-focusing and defocusing modify the wave front phase, thereby modifying the detected beam intensity (the setup is sketched in Fig. 3). The variation of the index of refraction $\Delta n(r, t)$, where r is the radial distance from the beam axis, can be written as the sum of terms that arise from the temperature change (ΔT), the volume-fraction change ($\Delta\phi$), and the light intensity $I(r, t)$ on the sample. Each process which takes place in the sample has its typical characteristic time: the Soret effect t_S ~ *seconds*; thermal lens effect t_c ~ ms; and electronic effects t_e ~ femtoseconds. So, Z-Scan experiments with different time-scale square waves can be used to study these different processes. The experimental results obtained until now with the FRS and ZS techniques can be summarized as follows:

I The sign of S_T depends on the sign of the charge of the surface particles;
II In water-based SFF, the thermodiffusive behavior is opposite to that of IFF; i.e., particles coated with cationic surfactants behave as negatively charged IFF (alkaline) particles, and particles coated with anionic surfactants behave as positively charged IFF (acid) particles;
III SFF with particles coated with nonionic surfactants dispersed in nonpolar fluid carriers behave as SFF with particles coated with cationic surfactants;
IV The nature of the liquid carrier itself is not the only determinant factor of the sign of *ST* , except in the case of the nonpolar fluids, where *ST* seems to be always positive.
In the case of the SFF (e.g., EMG607 from Ferrotec$^{\text{TM}}$, ZS experiments gave $S_T/\phi = 4.4\times10^{-3}K^{-1}$, where ϕ is the volume fraction of magnetic particles. In other words, S_T seems to be proportional to ϕ and, at $\phi = 0.45\times10^{-2}$, $S_T = (2.0\pm0.3)\times10^{-5}K^{-1}$. The proportionality between S_T and ϕ was verified in others SFF and IFF [20]. These results still lack a comprehensive theoretical picture and, probably, different mechanisms take place in the thermodiffusive behavior of these complex fluids [21]. Bringuier and Bourdon [22] prosed a kinetic theory, based on the analysis of a Brownian motion in a nonuniform temperature profile, in order to predict both signs of the Soret coefficient.

3. APPLICATIONS

Electronic devices

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 higher pressures.

Mechanical engineering

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

Aerospace

NASA has experimented using ferrofluids in a closed loop as the basis for a spacecraft's attitude control system. A magnetic field is applied to a loop of ferrofluid to change the angular momentum and influence the rotation of the spacecraft.

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.

Medicine : In medicine, ferrofluids are used as contrast agents for magnetic resonance imaging and can be used for cancer detection. The ferrofluids are in this case composed of iron oxide nanoparticles and called SPION, for "Superparamagnetic Iron Oxide Nanoparticles"There is also much experimentation with the use of ferrofluids in an experimental cancer treatment called magnetic hyperthermia. It is based on the fact that a ferrofluid placed in an alternating magnetic field releases heat.

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 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, 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 an efficient cooling method which requires no additional energy input

Optics: Research is under way to create an adaptive optics shape-shifting magnetic mirror from ferrofluid for Earth-based astronomical telescopes.[7]

Art: Some art and science museums have special devices on display that use magnets to make ferrofluids move around specially shaped surfaces in a fountain show-like fashion to entertain guests. Sachiko Kodama is known for her ferrofluid art.

The Australian electronic rock band, Pendulum, used ferrofluid for the music video for the track, Watercolour. The design house Krafted London was responsible for the ferrofluid FX in the video. The post-metal band Isis also uses a Ferrofluid in the music-video for 20 Minutes/40 Years.CZFerro, an American art studio, began using ferrofluid in its productions in 2008. The works consist of ferrofluid displayed in a unique suspension solution. These works are often used as conversation pieces for offices and homes.

A distinguishing feature of the research area in ferrofluids is the ample applicability of these materials. A big effort was made by chemists and physicists during a good part of last century to synthesize stable magnetic fluids, motivated by the perspective of many and important technological uses. Although non-stable suspensions of magnetic particles in liquids have been produced much earlier, the first synthesis of a ferrofluid was reported in the pioneering work by Papell , in 1965. After this, an increasing scientific production took place in the area. In Fig. 8 we reproduce a plot which we published [23] together with the bibliography on magnetic fluids for the Proceedings of the 10*th* International Conference on Magnetic Fluids, ICMF10, of the accumulated number of papers and patents published up to each year. A remarkable feature of this field is that the number of patents is about one half the number of papers, a clear confirmation to the perspective of ample applicability of ferrofluids.

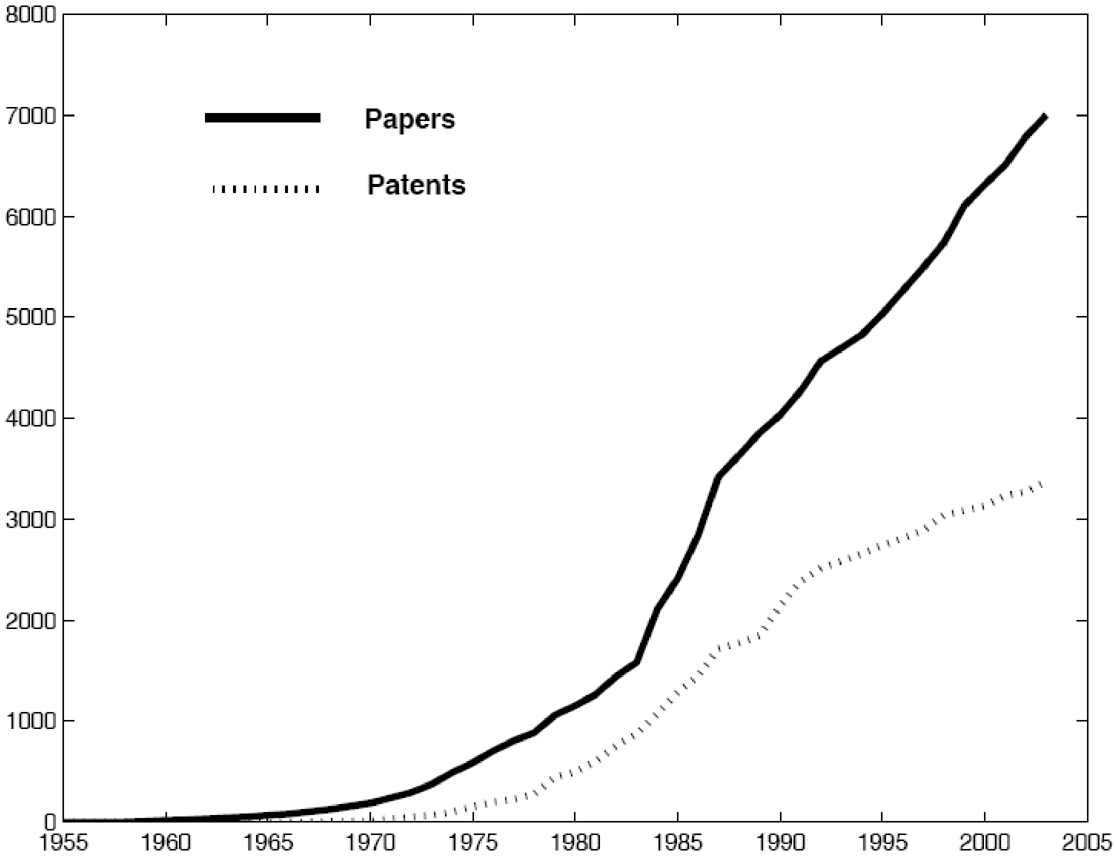

FIG. 4: Accumulated production of papers and patents on magnetic fluids up to every year.

The research field of magnetic fluids is a multi-disciplinary area: Chemists study their synthesis and produce the ferrofluids, Physicists study their physical properties and propose theories which explain them, Engineers study their applicability and use them in technological products, Biologists and Physicians study their biomedical possibilities and use them in Medicine and in research on the biological area.

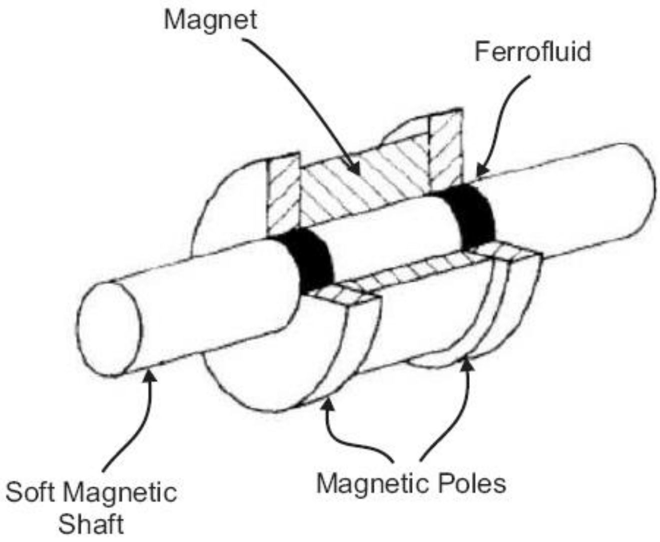

Fig. 5: Dynamic seal, reproduced from Raj and Moskowitz [23].

Most applications of magnetic fluid are based on the following of its properties:

1) It goes to where the magnetic field is strongest and stays there;
2) It absorbs electromagnetic energy at convenient frequencies and heats up;
3) Its physical properties may change with the application of a magnetic field;

These properties make the magnetic fluids useful for many technological, biological and medical purposes, as well as a help in materials science and engineering research. In the following sub-sections we comment on some of these applications.

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