Emergent Viscous Phenomena in Ferrofluids

Michael Murray

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Abstract

This essay investigates the magnetoviscous properties of ferrofluid flow in both an external magnetic field and in zero field. Zero-field properties of ferrofluids are examined. Phenomena such as the dramatic increase in ferrofluid viscosity in the presensce of a static field as well as "negative viscosity" for an alternating magnetic field are described.

Ferrofluids, or magnetic fluids, are suspensions of solid magnetic particles in a carrier fluid. They resemble salt solutions in that there are essentially floating magnetic moments free to move and rotate in a liquid. The reason ferrofluids yield interesting physics is the magnetic moment of a ferrofluid particle is three or four orders of magnitude larger than that of a salt ion. This means paramagnetic effects are amplified and new behaviors are seen.

Ferrofluids are not limited to academic research. They have found use in a number of commercial devices, such as lubrication spinning shafts that need to be air tight. A magnetic housing forces the ferrofluid to stay in place, maintaining the seal. This concept is used in computer hard drives. Another application is in tweeter speakers. The vibrating coil must be unattached to the speaker housing, but this does not allow conduction of heat to the body of the speaker. A ferrofluid held in place magnetically allows heat to dissipate, allowing the temperature of the voice coil to stay in a reasonable range for drastically higher power output.

This paper will not focus on these engineering applications, but rather magnetoviscous effects in ferrofluids, where the viscosity of ferrofluids is dramatically altered by the presence and direction of an external magnetic field. A static field oriented perpendicular to the vorticity of a fluid flow will increase the viscosity of a ferrofluid. Time-dependent, alternating magnetic fields will be discussed, and most interesting of all, a description of how viscosity can actually decrease via application of a magnetic field, known as "negative viscosity".

General properties of ferrofluids

Ferrofluids consist of ferromagnetic particles in a carrier fluid, typically oil or water. A wide range of particle diameters can be synthesized, and interesting effects are present from a few nanometers to micron-sized particles. A variety of materials can be used to make the ferromagnetic particles, but the most common is magnetite (Fe_3O_4). The first criterion for a feasible colloid is, of course, stability to sedimentation. Under the effect of gravity and applied magnetic fields, the particles will naturally clump in a prefered direction. In construction of a workable ferrofluid, the energy scale for gravitational and magnetic interactions must be much smaller than k_BT. This condition can be written as

$$k_BT > \mu H \tag{1}$$

where μ is the magnetic moment of the particles. In terms of the spontaneous magnetization of the particles, M_0, one obtains a condition on the diameter of the particles.

$$d < \left(\frac{6k_B T}{\mu_0 M_0 \pi H} \right)^{1/3} \tag{2}$$

where μ_0 is the Bohr magneton and H is the applied field. For typical field strengths at room temperature and the spontaneous magnetization of magnetite, this comes out to about $d_{max} = 6$ nm. A similar analysis can be done for gravitational sedimentation, giving $d_{max} = 10$ nm. (Odenbach, 2002)

Another source of attraction leads to problems - the magnetic dipole-dipole interaction. Avoiding this amounts to the condition that, for a particle separation of r,

$$2k_B T > \frac{\mu^2}{2\pi\mu_0} \frac{1}{r^3} \tag{3}$$

For the minimum separation of particles equal to their diameter, $r = d$, this is not a problem - the maximum diameter is at least as large as the maximum required by the sedimentation conditions. The real problem occurs when van der Waals forces cause many separate particles to agglomerate into a larger particle, the diameter of this agglomerate can exceed the maximum allowed for gravitational and external field sedimentation stability. To combat this, the magnetite particles are coated with polymeric surfactant which provide a steric repulsion force. This prevents the particles from lumping together and thus sedimenting.

While the energy scale arguments yield distance scales for the size of the particles, any real ferrofluid will have particles of a range of sizes and also a range of surfactant thicknesses. Much of the experimental work is limited in precision by the uncertainty in the actual sizes of the particles, as will be seen later. (Odenbach, 2002)

Magnetic susceptibility

Since the magnetic colloid particles are so small, they are made up of a single magnetic domain, which is easily calculated from the material properties and size of the particles. In order to find the magnetic susceptibility, one can use the well-known Langevin formula (Shliomis 1974)

$$M = M_0 \phi \left(\coth \left(\frac{\mu H}{k_B T} \right) - \frac{k_B T}{\mu H} \right) \tag{4}$$

where ϕ is the volume fraction of magnetic particles, and thus $M_0\phi$ is the magnetization of the ferrofluid as $H \to \infty$. For small fields, the initial susceptibility, χ_0 is found as

$$\chi_0 = \frac{M_0\phi}{3}\frac{\mu}{k_B T} \tag{5}$$

For a typical ferrofluid at volume fraction 7%, this will be on the order of $\chi_0 = 1$. Compare this to typical paramagnetic materials like iron oxide ($\chi = 7.2 \times 10^{-3}$) or ferromagnetic iron ($\chi \gtrsim 200$, depending on purity).

Relaxation to an external field

When an external field is applied or changed the magnetic particles will favor pointing along the field to minimize their alignment energy. This does not happen instantaneously, however, and the characteristic time scale is known as the relaxation time. For ferrofluid particles, conventionally, there are two pathways for relaxation. If the magnetic moment of the particles is fixed with respect to the crystal structure, the particles will relax via physical rotation. These are called magnetically hard particles and the process is Brownian relaxation. Also possible is a realignment of the magnetic field with respect to the crystal structure, leading to no physical rotation of the particles. These are magnetically weak particles and the process is Neél relaxation. The time scales for each of these are dependent on particle diameter, the anisotropy constant of the magnetic material, and the viscosity of the carrier fluid. Which relaxation process a particle follows is determined by the shorter of the two time scales as long as they are not of similar order. Obviously, for similar relaxation times, a combination of the two processes will occur. In an actual ferrofluid, the distribution in particle size can lead to different relaxation times for each particle, complicating the analysis. (Odenbach 2002)

Zero-field viscosity

Field dependent viscosity of a ferrofluid is an important property that will be examined later. Understanding the viscosity of a ferrofluid free of an external magnetic field is a prerequisite for any sort of non-zero field analysis. For a non-interacting suspension of particles, Einstein gave the colloidal viscosity, η_0 in terms of the carrier fluid viscosity,η_c and the volume fraction of everything suspended in the fluid, $\tilde{\phi}$.

$$\eta_0 = \eta_c\left(1 + \frac{5}{2}\tilde{\phi}\right) \tag{6}$$

This linear relation really is not accurate enough for any volume fraction above $\tilde{\phi} = 0.1$. Rosensweig extended this to higher order in $\tilde{\phi}$ by assuming that at some critical volume fraction, $\tilde{\phi}_c$, the viscosity should diverge - that is, the colloid becomes rigid. Using the volume fraction for close packed spheres for this critical volume fraction, $\tilde{\phi} = 0.74$, the relation for the viscosity becomes

$$\eta_0 = \eta_c \left(1 - \frac{5}{2}\tilde{\phi} + \left(\frac{5}{2}\tilde{\phi}_c - 1 \right) \left(\frac{\tilde{\phi}}{\tilde{\phi}_c} \right)^2 \right)^{-1} \tag{7}$$

This approximates the viscosity fairly well up until $\tilde{\phi} = 0.30$ or so. (Rosensweig, 1985)

Rotational viscosity

The physics is much more interesting when there is an applied external magnetic field. The viscosity is usually greater under the influence of a static field, but it will be shown that an alternating magnetic field can decrease the viscosity. In the extreme case, the viscosity can actually become negative - the magnetic field contributes to the rotation of particles, rather than hinder it.

Consider ferrofluid particles that are magnetically hard - their moments are fixed with respect to the crystal structure and they relax to a magnetic field via physical rotation of the particles. Also ignore any interaction between the particles - assume the suspension is dilute. Particles moving in a flow with vorticity will rotate in the same direction as the vorticity of the flow. The applied field will torque the particles towards lining up their magnetic moments with the field. If the magnetic field is in the same direction as the vorticity, the magnetic moments will line up with the vorticity and the particles will rotate about their magnetic moments. There is no further torque from the magnetic field, so the viscosity is left the same as with no field.

However, if the applied field is perpendicular to the vorticity, the magnetic torque again will attempt to line the particles up with the field. In contrast to this, though, the torque from the shear flow will try to misalign the particles with the field. These competing torques will create an anisotropic viscosity change dependent on the strength of the field. At a large enough applied field, the viscosity will be enough to entirely prevent the rotation of the particles.

For a theoretical treatment, see (Schliomis 1972). The particular setup worked out is Couette flow, or a fluid sandwiched between two plates with a relative velocity such that there is a shear. He begins with the Navier-Stokes equation

$$\rho\frac{d\vec{v}}{dt} = -\nabla\left[p + \frac{1}{2}\mu_0(\vec{M}\cdot\vec{H}) + \frac{\vec{S}}{I}(\vec{S} - I\vec{\Omega})\right] + \mu_0(\vec{M}\cdot\nabla)\vec{H} + \eta\nabla^2\vec{v} + \frac{I}{2\tau_s}\nabla\times(\vec{S} - I\vec{\Omega}) \tag{8}$$

and the torque equation for the change in angular momentum

$$\frac{d\vec{S}}{dt} = \mu_0\vec{M}\times\vec{H} - \frac{1}{\tau_s}(\vec{S} - I\vec{\Omega}) \tag{9}$$

Also needed is the rate of change of the magnetization of the particles when rotated relative to the field.

$$\frac{d\vec{M}}{dt} = \frac{1}{I}\vec{S}\times\vec{M} - \frac{1}{\tau_B}(\vec{M} - M_0\hat{H}) \tag{10}$$

The actual calculation of the viscosity as a function of field strength is too involved for this work, so the general strategy will be mentioned and the results quoted. First, assume stationary flow, $d\vec{S}/dt = 0$ and thus $d\vec{M}/dt = 0$. Then an expansion in $\vec{M}$ for small deviations around the equilibrium value linearizes the equations, allowing calculation of the force per unit volume. The viscosity term has an additional portion, referred to as the rotational viscosity, which is field dependent. He finds the rotational viscosity to be

$$\eta_r = \frac{3}{2}\phi\eta_0\frac{\xi - \tanh\xi}{\xi + \tanh\xi} \tag{11}$$

for a field perpendicular to the vorticity of the flow. Here $\xi = \frac{\mu H}{k_B T}$ is known as the Langevin parameter.

Examining this expresion in the high-field limit, $H \to \infty$, the fraction involving ξ goes to 1 and the maximum viscosity change is (remember ϕ is the volume fraction of the colloid particles).

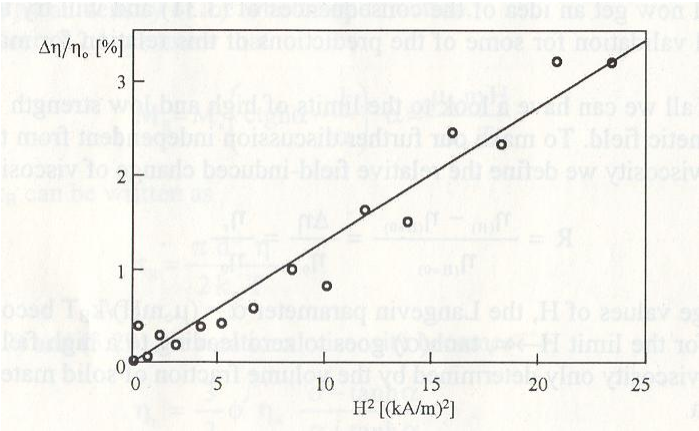
$$\frac{\eta_{r,max}}{\eta_0} \to \frac{3}{2}\phi \tag{12}$$

So there's only so much of a viscosity increase that can be provided by an increasing field.

In the low field limit, the ξ dependence can be approximated as $\xi^2/6$, giving the low field behavior as

$$\frac{\eta_r}{\eta_0} = \frac{1}{4}\phi\xi^2 = \frac{\mu^2\phi}{4(k_B T)^2}H^2 \tag{13}$$

The experimental fit for this can be seen in (Odenbach 2002, McTague 1969) and is reproduced here.



Negative viscosity

Next to consider is the case of a time-dependent magnetic field. The constant field gives an increased viscosity. One can easily envision a magnetic field rotating frequently enough that the hinderance to particle rotation is reduced to zero, and for even larger frequency fields, the particles are even sped up in their rotation.

According to (Shliomis 1994), the situation can be described with the Navier-Stokes equation,

$$\rho\frac{d\vec{v}}{dt} = -\nabla p + (\vec{M}\cdot\nabla)\vec{H} + \eta\nabla^2\vec{v} + \frac{I}{2\tau_s}\nabla\times(\vec{\Theta}-\vec{\Omega}) \tag{14}$$

the equation for the change in magnetization,

$$\frac{d\vec{M}}{dt} = \vec{\Theta}\times\vec{M} - \frac{1}{\tau_B}(\vec{M}-\vec{M_0}) \tag{15}$$

and the angular momentum relation for the particles.

$$I\frac{d\vec{\Theta}}{dt} = \vec{M}\times\vec{H} - \frac{I}{\tau_s}(\vec{\Theta}-\vec{\Omega}) \tag{16}$$

Here $\vec{\Theta}$ is the angular velocity of the particles, $\vec{\Omega}$ is the angular velocity of the vortex flow, τ_s is the time scale associated with colloid particles not matching the angular velocity of the flow, τ_B is the Brownian relaxation time, M_0 is the equilibrium magnetization, and the other variables are common to the fluid equation.

Considering the weak field case, $\mu H \ll k_B T$, the magnetic susceptibility can be approximated as linear. We are interested in the response to an applied alternating magnetic field, $H(t) = H_0 \cos(\omega t)$, which is decomposed into two counter-rotating fields, admitting an analytic solution.

First, the solution in which there is no fluid flow, but the magnetization lags the field with some angle α.

$$M = \frac{\xi H_0}{\sqrt{1+\omega^2\tau_B^2}} \tag{17}$$

$$\Theta = \omega \frac{\xi^2/3}{1+\omega^2\tau_B^2}$$

$$\tan\alpha = \omega\tau_B \left(1 - \frac{\xi^2/3}{1+\omega^2\tau_B^2}\right)$$

Remember that $\xi = \frac{\mu H}{k_B T}$ is the Langevin parameter. Since there is nothing to break the symmetry in the two counter rotating components of $H(t)$, half the particles rotate one way, and half the particles rotate the other way during a given cycle, resulting in no net fluid rotation. This is much less interesting than the case where there is vorticity, $\vec{\Omega} = \frac{1}{2}\nabla \times \vec{v}$. In this case, the counter-rotating components of the applied field don't have equal effect on the rotational velocity of the flow. Solving this case is more involved, so the reader is referred to Shliomis' derivation, and the result will be quoted here. The predicted change in viscosity, $\Delta\eta$ is given by

$$\Delta\eta = \frac{1}{4}\eta\phi\xi^2 \frac{1-\omega^2\tau_B^2}{(1+\omega^2\tau_B^2)^2} \tag{18}$$

Notice that for $\omega\tau_B > 1$ this change in viscosity is *negative* - the alternating magnetic field is actually driving the particles' rotation. A graph of the functional dependence of $\Delta\eta$ is shown.

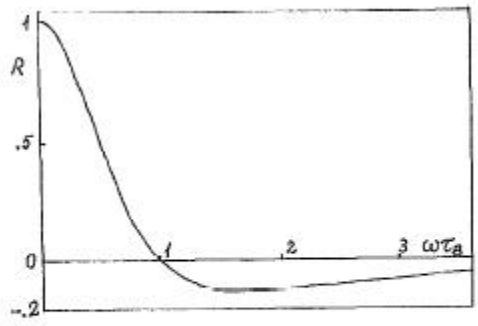


FIG. 1. The frequency dependence of the relative rotational viscosity $R=4\Delta\eta/(\eta\varphi\xi^2)$ for a low field ($\xi\ll 1$).

Experimental verification comes from (Bacri 1995). They used cobalt-ferrite particles suspended in water with a volume fraction of 20%. The particles were about 10 nm in diameter, and, due to the material properties, within the magnetically hard regime. They used transient birefringence to measure the Brownian relaxation time, τ_B. The experimental setup was a capillary viscometer exhibiting Poiseuille flow placed inside a solenoid. The magnitude of the field was 1 Oe and the frequency range probed was from 0 to 1 kHz.

The data show some agreement with theory, although the particular functional structure is not a perfect matchup. The phenomenon of negative viscosity for some parts of the field strength-frequency phase space is readily apparent, however.

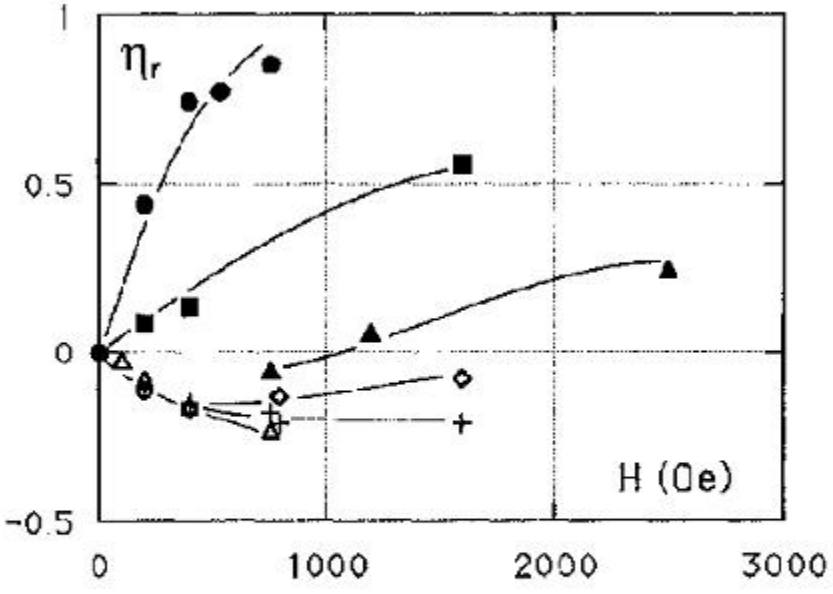


FIG. 2. Experimental reduced viscosity $\eta_r(H,f) = [\eta(H,f) - \eta(0,0)]/\eta(0,0)$ versus magnetic field H for different frequencies f : ●: $f = 0$; ■: $f = 52$ Hz; ▲: $f = 150$ Hz; ◇: $f = 345$ Hz; +: $f = 645$ Hz; and ∧: $f = 1480$ Hz. Full lines are guides for the eye.

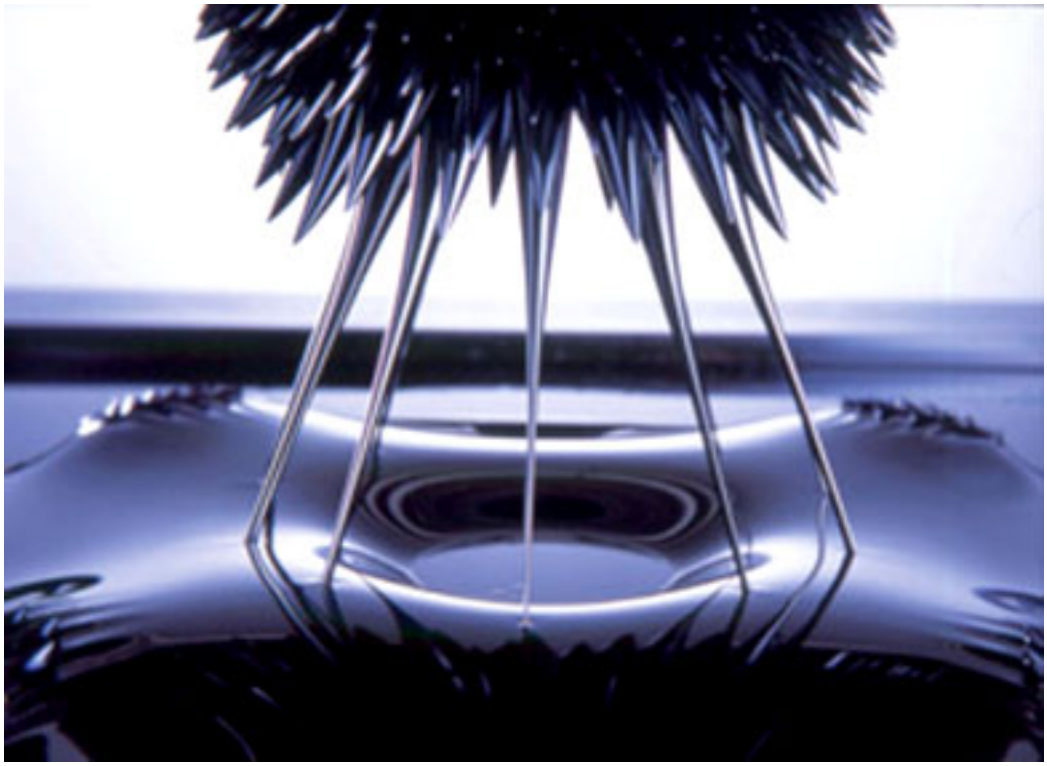
The vertical axes in these plots are scaled differently, and the horizontal axis is frequency in the first, field strength in the second, so it's difficult to do any sort of functional comparison by eye. Notice though the negative viscosity region in both.

Conclusion and further interest

In this paper, the principles of viscosity control via magnetic fields applied to ferrofluids has been illustrated. Application of a static magnetic field can be used to increase the viscosity of a ferrofluid. This has application in controlled damping of suspension systems. With dynamic viscosity control, more comfortable and smooth damping can be achieved by altering the damping coefficient through the oscillation. Ferrofluids also exhibit "negative viscosity", where the rotational viscosity can actually decrease the overall viscosity of the fluid from the non-rotating value.

Some of the more interesting properties of ferrofluids have little practical application, but are stunning to watch. The reader is recommeded to search on YouTube or

procure video footage of the Rosensweig instability in ferrofluids. A static magnetic field applied perpendicular to the surface of a ferrofluid will cause a formation of spikes that hang in mid air. A combination of surface tension, gravity, and magnetic forces combine to produce this strange looking phenomenon. Also interesting is the labyrinthine pattern formation of ferrofluids. The analysis of these effects is a current research topic, and a difficult problem. There is theoretical work on the subject, especially in the area of linear stability analyis. Unfortunately, the analysis is far too complicated and lengthy to be a part of the scope of this work.



Electromagnet above the field of view, showing the characteristic spike pattern.

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