Analysis of Superparamagnetic Materials

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Introduction

In F. Martin-Hernandex et. al. (Tectonophysics 418 (2006) 21-30) we find excellent data on magnetite for very small physical sizes found in common ferrofluids. What makes magnetite interesting on these scales is that it acts like a perfect superparamagnetic material. It has no hysterisis, no coercivity and responds on gigahertz time scales. The data shows magnetite with magnetic saturation as a function of temperature and a $B_{1/2}$ of 0.015 Tesla. Fitting a curve to the data I find the following:

$$M(B) = M_s\left(\frac{1-3^{-B/B_{1/2}}}{1+3^{-B/B_{1/2}}}\right) \tag{1}$$

The assumption is that the direction of magnetic polarization is along $\vec{B}$, but this is only true for time scales much longer than the relaxation time. For details see "Surface Contributions to the Anisotropy Energy of Spherical Magnetite Particles¨, www.physics.montana.edu/students/gilmore/surface-draft.pdf. From that paper I find the time constant to be about 0.38 nsec.

For optical problems which we wish to solve in the future, the frequency of interest is closer to 10^{14} Hz. At thise frequencies, magnetite on these dimensions (nm) does not respond at all magneticly. This is counter intuitive. A good picture is to view the magnetite as a uniform distribution which locks onto the external field and can not change its lock on the order of the relaxation time. The dielectric properties still follow the unlocked electrons, but the electrons which participate in the magnetic behavior are stuck to the external static field.

Unlike ferromagnets which maintain their lock even when the external field is removed, magnetite is superparamagnetic which means it has no H_c even after the external field is removed. This is discussed in many areas of literature (see above references). However, because it is superparamagnetic, magnetite responds rapidly to even a weak steady external field. This is only true for ferrofluid sized particles, and I will begin with a slightly hand waving form of argument before delving into the solution.

Physics of ferrofluid particles

Let's begin with a close look at magnetite. It is composed of 3 iron and 4 oxygen molecules arranged in a "spinel" complex. Two of the iron atoms have +3 charge, and one has +2. It is a ferrite because the same charged atoms have their magnetic moments opposing each other, and the third is left to define the magnetic moment of the cell. The exact structure of magnetite is not fully understood because it changes from an insulator to a metal at 125 Kelvin and goes from magnetic to paramagentic at about 900 K (quite a bit higher than most other ferrites). A "cell" is some what loosely defined. But most data show that it is around 2.5 Å.

The magnetic moment of all magnetic materials is given in the number of Bohr magneton equivelents. A Bohr magneton is defined as

$$\mu_B = \frac{eh}{4\pi m} \qquad (2$$

where e is the charge on an electron, m is the mass of an electron and h is Plank's constant. Plugging in numbers we find $\mu_B = 9.274 \times 10^{-24}$ J/T. (That's Joules per Tesla.) Kittel (Introduction to Solid State Physics) says magnetite has around 4.1 μ_B per cell or 3.8×10^{-23} J/T.

The field from a dipole is given in Jackson (Classical Electrodynamics) as

$$B \approx \frac{\mu_0}{4\pi} \frac{\eta}{r^3} \qquad (3$$

times angular functions. Here μ_0 is permiability of free space, η is magnetic moment ($4.1\,\mu_B$) and r is the distance from the center of the dipole to the point in question. I'm only interested in handwaving here, so only magnitude is required.

Magnetite is a cubic lattice, so each dipole has 6 nearest neighbors at $r_0 = 2.5$Å, 12 neighbors at $r_1 = \sqrt{2} r_0$ and 8 neighbors at $r_2 = \sqrt{3} r_0$. Putting these numbers into the above equation we find the maximum possible field from neighbors is 1.46T, 1.03T and 0.37T for r_0, r_1, and r_2 respectively. The total energy available is then 1.1×10^{-22} J.

As stated in the "Surface Contributions..." article, the anisotropy energy of magnetite is around 10^{-14} ergs which is 10^{-21} J. So from a pure energy argument we see that the lack of ability to lock the magnetite into a magnet is coming from the energy available from each cell. The local magnetic fields are too small to affect the whole particle.

This allows us to make the following most important assumption: The field inside a ferrofluid particle is only created by external influence. There is no self field generated.

Formula expansion

Equation 1 gives a description of magnitude. To find fields which are vectors we must make an assumption about the field direction. Magnetite is anisotropic, but for our purposes we will assume that it is uniform and that the magnitude response is along the field line. Since most small particles are reasonably spherical, I use spherical coordinates. Equation 1 becomes:

$$\vec{M}(\vec{B}) = M_s \left(\frac{1 - 3^{-B/B_{1/2}}}{1 + 3^{-B/B_{1/2}}} \right) \frac{\vec{B}}{B} \qquad (4$$

where $\vec{B} = B_r \hat{r} + B_\theta \hat{\theta} + B_\phi \hat{\phi}$ and $B = (B_r^2 + B_\theta^2 + B_\phi^2)$. (5

If we have an external field $\vec{B} = B_0 \hat{z} = B_0(\cos\theta \hat{r} - \sin\theta \hat{\theta})$ at a distance far away from the central spherical particle, we can then attempt to find the magnetic field near the particle as it responds to this distant field using Maxwell's equations. The fundamental equations inside the magnetite are:

$$\vec{\nabla} \bullet \vec{B} = 0 \qquad (6$$

$$\vec{B} = \mu_0 \left(\vec{H} + \vec{M}(B) \right) \qquad (7$$

and because there are no currents

$$\vec{\nabla} \times \vec{H} = 0 \qquad (8$$

Combining equations 4, 7 and 8 we get

$$\vec{\nabla} \times \left(\frac{\vec{B}}{\mu_0} - M_s \left(\frac{1 - 3^{-B_0/B_{1/2}}}{1 + 3^{-B_0/B_{1/2}}} \right) \frac{\vec{B}}{B_0} \right) = 0 \qquad (9$$

Since the magnitude of the field inside the particle can only be created by the external field we have a great simplification so that equation (9 becomes

$$\left[\frac{1}{\mu_0} - \frac{M_s}{B_0} \left(\frac{1 - 3^{-B_0/B_{1/2}}}{1 + 3^{-B_0/B_{1/2}}} \right) \right] \vec{\nabla} \times \vec{B} = 0 \qquad (10$$

Along with boundary conditions, equation 10 allows us to solve for $\vec{B}$ everywhere.

The boundary condition is tangenetial $\vec{H}$ is continous (because there are no currents present). The above equation 10 is for inside the magnetite. Outside we have simply

$$\vec{\nabla} \times \vec{B} = \frac{1}{r\,\sin\theta} \left[\frac{\partial}{\partial\theta}(\sin\theta B_\phi) - \frac{\partial B_\vartheta}{\partial\phi} \right] \hat{r} + \left[\frac{1}{r\,\sin\theta} \frac{\partial B_r}{\partial\phi} - \frac{1}{r} \frac{\partial(\mathrm{rB}_\phi)}{\partial r} \right] \hat{\theta} + \frac{1}{r} \left[\frac{\partial(\mathrm{rB}_\theta)}{\partial r} - \frac{\partial B_r}{\partial\theta} \right] \hat{\phi} = 0 \qquad (11$$

But really equation 11 and 10 are the same since we can divide the constant out in front. If the magnetude of $\vec{B}$ inside the magnetite did depend on self generated fields, we would have a far more complicated problem.

In spherical coordinates, equation 6 is

$$\frac{1}{r^2} \frac{\partial}{\partial r}(r^2 B_r) + \frac{1}{r\,\sin\theta} \frac{\partial}{\partial\theta}(\sin\theta B_\theta) + \frac{1}{r\,\sin\theta} \frac{\partial B_\phi}{\partial\phi} = 0 \qquad (12$$

and is true both inside and outside the material.

Breaking up the components of equation 11 gives the following:

$$\frac{\partial}{\partial\theta}(\sin\theta B_\phi) - \frac{\partial B_\theta}{\partial\phi} = 0 \qquad (13$$

$$\frac{1}{\sin\theta} \frac{\partial B_r}{\partial\phi} - \frac{\partial(\mathrm{rB}_\phi)}{\partial r} = 0 \qquad (14$$

$$\frac{\partial(\mathrm{rB}_\theta)}{\partial r} - \frac{\partial B_r}{\partial\theta} = 0 \qquad (15$$

At this point we need to consider the fields inside and outside as separate, so some variarable naming is in order here.

Uniform external field

If we make the assumption that an external magnetic field is created which is both large and far from the very small magnetite particle, then a uniform field as $r \to \infty$ can be described with

$$\vec{B} = B_0\hat{z} = B_0(\cos\theta\hat{r} - \sin\theta\hat{\theta}) \qquad (16$$

Note that this satisfies equations 12-15 with $B_r = B_0\cos\theta$ and $B_\theta = -B_0\sin\theta$. To keep inside and outside straight, from here on I will use capital B for outside and lower case b for inside fields. With this notation we can write the boundary conditions on the surface of the magnetite as

$$B_\theta|_{r=d/2} = b_\theta|_{r=d/2} \qquad (17$$

where d is the diameter of the sphere. The tangential components will be

$$B_t = b_t' - \mu_0 M_t(B_0) \qquad (18$$

where the subscript t is for tangential. For the specific case of spherical particles we have (letting $a = B_{1/2}^{-1}$)

$$B_\theta = b_\theta' - \mu_0 M_s \frac{1-3^{-aB_0}}{1+3^{-aB_0}}\sin\theta \qquad (19$$

$$B_\phi = b_\phi \qquad (20$$

and the evaluation is at the boundary $r = d/2$. Now, we can simplify a lot because the field in equation 16 is independent of ϕ. The derivatives with respect to ϕ are all exactly zero, and by symmetry we can see that B_ϕ must be zero everywhere. By equation 20, we must also have b_ϕ zero on the boundary, and by extension (from 6 and 12) within the sphere as well. In the more general case with many particles near each other, the far field conditions will not be so simple.

We now have 4 unknowns: B_r, B_θ, b_r, and b_θ. The four equations which determine these variables are 15 and 12 for the outside field, and the corresponding inside versions of 15 and 12 with lower case variables. The reason is that there is simply a constant multiplying $\nabla \times \vec{B}$ in equation 15. We can rewrite these equations without the rotational component in the ϕ direction and our problem becomes two dimensional.

From 15 we have

$$B_\theta + r\frac{\partial B_\theta}{\partial r} - \frac{\partial B_r}{\partial \theta} = 0 \qquad (21$$

From 12 we get (for outside variables)

$$\frac{2}{r}B_r + \frac{\partial B_r}{\partial r} + \frac{\cot\theta}{r}B_\theta + \frac{1}{r}\frac{\partial B_\theta}{\partial \theta} = 0 \qquad (22$$

and from 12 for inside variables

$$\frac{2}{r}b_r + \frac{\partial b_r}{\partial r} + \frac{\cot\theta}{r}b_\theta + \frac{1}{r}\frac{\partial b_\theta}{\partial \theta} = 0 \qquad (23$$

and finally equation 10 has only one term like 21 namely

$$\left[\frac{1}{\mu_0} - M_s\left(\frac{1-3^{-aB_0}}{1+3^{-aB_0}}\right)\right]\left(\frac{b_\theta}{r} + \frac{\partial b_\theta}{\partial r} - \frac{1}{r}\frac{\partial b_r}{\partial \theta}\right) = 0 \qquad (24$$

We see that equation 24 is identical to 21 by simply dividing out the constant (and multiplying by r). Thus we can solve all field equations with one method and use

$$\vec{b} = \mu_0\left(\vec{H} + M_s\left(\frac{1-3^{-a\,B_0}}{1+3^{-a\,B_0}}\right)\vec{B_0}\right) \qquad (25$$

to find the final solution inside.

Free space equations

Let's begin by rewriting 21 and 22 in their original forms

$$\frac{\partial(\mathrm{rB}_\theta)}{\partial r} = \frac{\partial B_r}{\partial \theta} \qquad (26$$

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r^2 B_r\right) = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\, B_\theta) \qquad (27$$

These two equations will allow separation of variables. We take

$$B_\theta = \mathcal{B}_\theta(r)\mathfrak{B}_\theta(\theta) \qquad (28$$

$$B_r = \mathcal{B}_r(r)\mathfrak{B}_r(\theta) \qquad (29$$

Putting 28 and 29 into 26 and 27 we find after a bit of manipulation

$$\frac{1}{\mathcal{B}_r}\frac{\partial}{\partial r}(r\mathcal{B}_\theta) = \frac{1}{\mathfrak{B}_\theta}\frac{\partial\mathfrak{B}_r}{\partial\theta} \qquad (30$$

$$\frac{1}{r\mathcal{B}_\theta}\frac{\partial}{\partial r}\left(r^2\mathcal{B}_r\right) = -\frac{1}{\sin\theta\,\mathfrak{B}_r}\frac{\partial}{\partial\theta}(\sin\theta\,\mathfrak{B}_\theta) \qquad (31$$

In both equations 30 and 31 the right and left hand sides are functions of just r and θ respectively. Since these are independant variables, all terms must be equal to some constant. Let the terms in equation 30 be equal to the constant β and the terms in equation 31 be equal to the constant γ.

For the radial equations we have

$$\frac{\partial}{\partial r}(r\mathcal{B}_\theta) = \beta\mathcal{B}_r \qquad (32$$

$$\frac{\partial}{\partial r}\left(r^2\mathcal{B}_r\right) = \gamma r\mathcal{B}_\theta \qquad (33$$

Putting 33 into 32 we find

$$\frac{\partial^2}{\partial r^2}\left(r^2\mathcal{B}_r\right) - \beta\gamma\mathcal{B}_r = 0 \qquad (34$$

A transformation of variables with $T = r^2\mathcal{B}_r$ turns 34 into

$$\frac{\partial^2 T}{\partial r^2} - \frac{\beta\gamma}{r^2}T = 0 \qquad (35$$

Since this is an equidimensional differential equation we can take $T = \mathrm{A}r^k$ which gives the characteristic equation

$$k(k+1) - \beta\gamma = 0 \qquad (36$$

Solving for k we find

$$k = \frac{1 \pm \sqrt{1+4\beta\gamma}}{2} \qquad (37$$

Solving for $\mathcal{B}_r$ from T gives

$$\mathcal{B}_r = \mathrm{A}r^{\frac{-3+\sqrt{1+4\beta\gamma}}{2}} + Dr^{\frac{-3-\sqrt{1+4\beta\gamma}}{2}} \qquad (38$$

From equation 33 and the definition for T we have $\gamma r \mathcal{B}_\theta = \frac{\partial T}{\partial r}$ so solving for $\mathcal{B}_\theta$ we find

$$\mathcal{B}_\theta = \frac{1}{2\gamma}\left[A\left(1+\sqrt{1+4\beta\gamma}\right)r^{\frac{-3+\sqrt{1+4\beta\gamma}}{2}} + D\left(1-\sqrt{1+4\beta\gamma}\right)r^{\frac{-3-\sqrt{1+4\beta\gamma}}{2}}\right] \qquad (39$$

Equations 38 and 39 are the general radial solutions to any 2D spherical problem of the form described by equations 21 and 22. We now turn our attention to the angular portion of the problem using the same constants β and γ in equations 35 and 36.

From the right hand sides of 30 and 31 we find

$$\frac{\partial \mathfrak{B}_r}{\partial \theta} = \beta \mathfrak{B}_\theta \qquad (40$$

$$\frac{\partial}{\partial \theta}(\sin\theta\, \mathfrak{B}_\theta) = -\gamma \sin\theta\, \mathfrak{B}_r \qquad (41$$

Putting 40 into 41 we get

$$\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \mathfrak{B}_r}{\partial \theta}\right) = -\beta\gamma \sin\theta\, \mathfrak{B}_r \qquad (42$$

We now do the standard change of variables with

$$x = \cos\theta \qquad (43$$

so that $\frac{\partial}{\partial\theta} = -\sin\theta \frac{\partial}{\partial x}$ which transforms equation 42 into the form

$$\frac{\partial}{\partial x}\left((1-x^2)\frac{\partial}{\partial x}\mathfrak{B}_r\right) + \beta\gamma\, \mathfrak{B}_r = 0 \qquad (44$$

which comes from $\sin^2\theta = 1 - \cos^2\theta = 1 - x^2$. From I. S. Gradshteyn & I. M. Ryzhik, “Table of Integrals, Series, and Products”, 1980 edition under section 8.820 we find that this matches Legendre functions so long as

$$\beta\gamma = \nu(\nu+1) \qquad (45$$

and the solution to 44 is given by

$$\mathfrak{B}_r = CP_\nu(\cos\theta) + GQ_\nu(\cos\theta) \qquad (46$$

To solve for $\mathfrak{B}_\theta$ we use some well known properties listed in Gradshteyn & Ryzhik, specifically 8.832.1 and 8.832.3 which give

$$(x^2-1)\frac{d}{dx}P_\nu(x)=(\nu+1)[P_{\nu+1}(x)-xP_\nu(x)] \quad (47$$

$$(x^2-1)\frac{d}{dx}Q_\nu(x)=(\nu+1)[Q_{\nu+1}(x)-xQ_\nu(x)] \quad (48$$

From the transformations $\frac{\partial}{\partial\theta}=-\sin\theta\frac{\partial}{\partial x}$ and $-\sin^2\theta=x^2-1$ we can convert equation 40 into

$$\sin\theta\frac{\partial\mathfrak{B}_r}{\partial\theta}=(x^2-1)\frac{\partial\mathfrak{B}_r}{\partial x}=\beta\sin\theta\,\mathfrak{B}_\theta \quad (49$$

With formulas 46, 47 and 48 we can solve for $\mathfrak{B}_\theta$ in 49. This gives

$$\mathfrak{B}_\theta=\frac{1}{\beta}\frac{\partial\mathfrak{B}_r}{\partial\theta}=\frac{\nu+1}{\beta\sin\theta}[CP_{\nu+1}(\cos\theta)+GQ_{\nu+1}(\cos\theta)-\cos\theta(CP_\nu(\cos\theta)+GQ_\nu(\cos\theta))] \quad (50$$

We can now combine equations 38 and 46 to get the solution for B_r and equations 39 and 50 for B_θ. We substitute $\beta\gamma=\nu(\nu+1)$ in all these equations and get the final result

$$B_r(r,\theta)=\left(\mathrm{Ar}^{\frac{-3+\sqrt{1+4\nu(\nu+1)}}{2}}+Dr^{\frac{-3-\sqrt{1+4\nu(\nu+1)}}{2}}\right)(CP_\nu(\cos\theta)+GQ_\nu(\cos\theta)) \quad (52(47(51$$

$$B_\theta(r,\theta)=\frac{1}{2\nu\sin\theta}\left[A\left(1+\sqrt{1+4\nu(\nu+1)}\right)r^{\frac{-3+\sqrt{1+4\nu(\nu+1)}}{2}}+D\left(1-\sqrt{1+4\nu(\nu+1)}\right)r^{\frac{-3-\sqrt{1+4\nu(\nu+1)}}{2}}\right][CP_{\nu+1}(\cos\theta)+GQ_{\nu+1}(\cos\theta)-\cos\theta(CP_\nu(\cos\theta)+GQ_\nu(\cos\theta))] \quad (52$$

Far field conditions

Equation 16 describes the form we expect in the limit $r\to\infty$. In M. Abramowitz and I. Stegun, "Handbook of Mathematical Functions" , Dover 1972, section 8.4 we find the following formulas for Legendre polynomials

$$P_1=\cos\theta \qquad Q_1=\frac{x}{2}\ln\left(\frac{1+x}{1-x}\right)-1$$

$$P_2=\frac{1}{2}(3\cos^2\theta-1)$$

It's really obvious that the Q's don't work in the limit for large r, so G must be zero. From equation 16 we see that

$$B_r=B_0\cos\theta \quad (53$$

can be satisfied exactly if $\nu=1$ because equation 51 becomes

$$B_r=\left(A+\frac{D}{r^3}\right)\cos\theta \quad (54$$

in the limit $r \to \infty$ 54 reduces to 53 and $A = B_0$. This fixes the solution for B_θ to be (from equation 52)

$$B_\theta = \frac{1}{2\sin\theta}\left[4B_0 - 2\frac{D}{r^3}\right]\left[\frac{1}{2}(3\cos^2\theta - 1) - \cos^2\theta\right] \qquad (55$$

With a little algebra we find that this reduces to

$$B_\theta = -\sin\theta\left(B_0 - \frac{D}{2r^3}\right) \qquad (56$$

Which is exactly what we need to meet the $r \to \infty$ conditions of the boundary condition from equation 16.

Near field equations

Equations 54 and 56 tell us the general form we need to apply to the internal field. The only difference is that we now have a constant term as seen from equations 7 and 19. This general form is

$$b_r = -\cos\theta\left[d_1 + \frac{d_2}{r^3} - \mu_0 M_s\left(\frac{1 - 3^{-aB_0}}{1 + 3^{-aB_0}}\right)\right] \qquad (57$$

and

$$b_\theta = \sin\theta\left[d_1 - \frac{d_2}{2r^3} - \mu_0 M_s\left(\frac{1 - 3^{-aB_0}}{1 + 3^{-aB_0}}\right)\right] \qquad (58$$

This must be valid at $r = 0$ so we see that $d_2 = 0$ is the only possible value for that coefficient. In the limit that $M_s \to 0$ (i.e. no material there at all) we need to recover a valid physical result. This happens trivially with $d_1 = -B_0$. We now have the complete solution for the field inside the sphere:

$$b_r = \cos\theta\left[B_0 + \mu_0 M_s\left(\frac{1 - 3^{-aB_0}}{1 + 3^{-aB_0}}\right)\right] \qquad (59$$

and

$$b_\theta = -\sin\theta\left[B_0 + \mu_0 M_s\left(\frac{1 - 3^{-aB_0}}{1 + 3^{-aB_0}}\right)\right] \qquad (60$$

Equations 60 and 56 can now be set equal to each other at $r = d/2$ as in equation 17. We find after moving terms around

$$D = 2\mu_0\left(\frac{d}{2}\right)^3 M_s\left(\frac{1 - 3^{-aB_0}}{1 + 3^{-aB_0}}\right) \qquad (61$$

Thus, the fields in space in and around the particle in a uniform field are now known completely. We have externally

$$\vec{B} = \left[B_0 + \frac{\mu_0 d^3 M_s}{4r^3}\left(\frac{1 - 3^{-aB_0}}{1 + 3^{-aB_0}}\right)\right]\cos\theta\,\hat{r} - \left[B_0 + \frac{\mu_0 d^3 M_s}{8r^3}\left(\frac{1 - 3^{-aB_0}}{1 + 3^{-aB_0}}\right)\right]\sin\theta\,\hat{\theta} \qquad (62$$

and internally

$$\vec{b} = \left[B_0 + \mu_0 M_s\left(\frac{1 - 3^{-aB_0}}{1 + 3^{-aB_0}}\right)\right]\cos\theta\,\hat{r} - \left[B_0 + \mu_0 M_s\left(\frac{1 - 3^{-aB_0}}{1 + 3^{-aB_0}}\right)\right]\sin\theta\,\hat{\theta} \qquad (63$$

Careful comparison of equations 62 and 63 show that the external field appears as a dipole centered on the particle for distances larger than the particle radius, and the internal field is constant and in the $\vec{z}$ direction as is the external fixed field.

Since the particles are so small, the assumption of a fixed external field is not a loss of generality. However, if anyone wants to, the full multipole expansion is available in the above equations to match more complex initial conditions.