Analysis of Superparamagnetic Materials

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:

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

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 Sphereical 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 each other.

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 repidly to even a weak steady external field. The first problem to be presented here, is a description of how equation 1 gives a rather complex response to external fields.

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:

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

where $\vec{B} = B_r\hat{r} + B_\theta\hat{\theta} + B_\phi\hat{\phi}$ and $B = (B_r^2 + B_\theta^2 + B_\phi^2)$. (3

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:

$$\vec{\nabla}\bullet\vec{B} = 0 \qquad (4$$

$$\vec{B} = \mu_0\left(\vec{H} + \vec{M}(B)\right) \qquad (5$$

and because there are no currents

$$\vec{\nabla} \times \vec{H} = 0 \qquad (6$$

Combining equations 2, 5 and 6 we get

$$\vec{\nabla} \times \left(\frac{\vec{B}}{\mu_0} - M_s\left(\frac{1-3^{-B/B_{1/2}}}{1+3^{-B/B_{1/2}}}\right)\frac{\vec{B}}{B}\right) = 0 \qquad (7$$

From the identity $\vec{\nabla} \times \left(\alpha\vec{A}\right) = \alpha\vec{\nabla} \times \vec{A} + \vec{\nabla}\alpha \times \vec{A}$ we can rewrite equation 7 as

$$\left[\frac{1}{\mu_0} - \frac{M_s}{B}\left(\frac{1-3^{-B/B_{1/2}}}{1+3^{-B/B_{1/2}}}\right)\right]\vec{\nabla} \times \vec{B} - \vec{\nabla}\left[\frac{M_s}{B}\left(\frac{1-3^{-B/B_{1/2}}}{1+3^{-B/B_{1/2}}}\right)\right] \times \vec{B} = 0 \qquad (8$$

Along with boundary conditions, equation 8 allows us to solve for $\vec{B}$ everywhere.

The boundary conditions are normal $\vec{B}$ is continuous and tangenetial $\vec{H}$ is continous (because there are no currents present). The above equation 8 is for inside the magnetite. Outside we have simply

$$\vec{\nabla} \times \vec{B} = \frac{1}{r\sin\theta}\left[\frac{\partial}{\partial\theta}(\sin\theta B_\phi) - \frac{\partial B_\vartheta}{\partial\phi}\right]\hat{r} + \left[\frac{1}{r\sin\theta}\frac{\partial B_r}{\partial\phi} - \frac{1}{r}\frac{\partial(\mathrm{r}\mathrm{B}_\phi)}{\partial r}\right]\hat{\theta} + \frac{1}{r}\left[\frac{\partial(\mathrm{r}\mathrm{B}_\theta)}{\partial r} - \frac{\partial B_r}{\partial\theta}\right]\hat{\phi} \qquad (9$$

Grinding through a whole lot of algebra we find (letting $a = B_{1/2}^{-1}$)

$$\vec{\nabla}\left[\frac{M_s}{B}\left(\frac{1-3^{-aB}}{1+3^{-aB}}\right)\right] = \left[-\frac{M_s}{B^3}\left(\frac{1-3^{-aB}}{1+3^{-aB}}\right) + 2\frac{M_s a\ln 3\, 3^{-\mathrm{aB}}}{B^2(1+3^{-\mathrm{aB}})^2}\right]\left[\left(B_r\frac{\partial B_r}{\partial r} + B_\theta\frac{\partial B_\theta}{\partial r} + B_\phi\frac{\partial B_\phi}{\partial r}\right)\hat{r} + \frac{1}{r}\left(B_r\frac{\partial B_r}{\partial\theta} + B_\theta\frac{\partial B_\theta}{\partial\theta} + B_\phi\frac{\partial B_\phi}{\partial\theta}\right)\hat{\theta} + \frac{1}{r\sin\theta}\left(B_r\frac{\partial B_r}{\partial\phi} + B_\theta\frac{\partial B_\theta}{\partial\phi} + B_\phi\frac{\partial B_\phi}{\partial\phi}\right)\hat{\phi}\right] \qquad (10$$

To get the final terms in equation 8 we take the cross product of equation 10 with $\vec{B}$ to find

$$0 = \left[\frac{1}{\mu_0} - \frac{M_s}{B}\left(\frac{1-3^{-aB}}{1+3^{-aB}}\right)\right]\frac{1}{r\sin\theta}\left[\frac{\partial}{\partial\theta}(\sin\theta\, B_\phi) - \frac{\partial B_\vartheta}{\partial\phi}\right] + \left[-\frac{M_s}{B^3}\left(\frac{1-3^{-aB}}{1+3^{-aB}}\right) + 2\frac{M_s a\ln 3\, 3^{-\mathrm{aB}}}{B^2(1+3^{-\mathrm{aB}})^2}\right]\left\{\frac{B_\phi}{r}\left(B_r\frac{\partial B_r}{\partial\theta} + B_\theta\frac{\partial B_\theta}{\partial\theta} + B_\phi\frac{\partial B_\phi}{\partial\theta}\right) - \frac{B_\theta}{r\sin\theta}\left(B_r\frac{\partial B_r}{\partial\phi} + B_\theta\frac{\partial B_\theta}{\partial\phi} + B_\phi\frac{\partial B_\phi}{\partial\phi}\right)\right\} \qquad (11$$

which comes from the $\hat{r}$ term,

$$0 = \left[\frac{1}{\mu_0} - \frac{M_s}{B}\left(\frac{1-3^{-aB}}{1+3^{-aB}}\right)\right]\left[\frac{1}{r\sin\theta}\frac{\partial B_r}{\partial\phi} - \frac{1}{r}\frac{\partial(\mathrm{r}\mathrm{B}_\phi)}{\partial r}\right] + \left[-\frac{M_s}{B^3}\left(\frac{1-3^{-aB}}{1+3^{-aB}}\right) + 2\frac{M_s a\ln 3\, 3^{-\mathrm{aB}}}{B^2(1+3^{-\mathrm{aB}})^2}\right]\left\{\frac{B_r}{r\sin\theta}\left(B_r\frac{\partial B_r}{\partial\phi} + B_\theta\frac{\partial B_\theta}{\partial\phi} + B_\phi\frac{\partial B_\phi}{\partial\phi}\right) - B_\phi\left(B_r\frac{\partial B_r}{\partial r} + B_\theta\frac{\partial B_\theta}{\partial r} + B_\phi\frac{\partial B_\phi}{\partial r}\right)\right\} \qquad (12$$

which comes from the $\hat{\theta}$ term, and finally

$$0=\left[\frac{1}{\mu_0}-\frac{M_s}{B}\left(\frac{1-3^{-aB}}{1+3^{-aB}}\right)\right]\frac{1}{r}\left[\frac{\partial(\mathrm{rB}_\theta)}{\partial r}-\frac{\partial B_r}{\partial\theta}\right]+\left[-\frac{M_s}{B^3}\left(\frac{1-3^{-aB}}{1+3^{-aB}}\right)+2\frac{M_s a\ln 3 3^{-\mathrm{aB}}}{B^2(1+3^{-\mathrm{aB}})^2}\right]\left\{B_\theta\left(B_r\frac{\partial B_r}{\partial r}+B_\theta\frac{\partial B_\theta}{\partial r}+B_\phi\frac{\partial B_\phi}{\partial r}\right)-\frac{B_r}{r}\left(B_r\frac{\partial B_r}{\partial\theta}+B_\theta\frac{\partial B_\theta}{\partial\theta}+B_\phi\frac{\partial B_\phi}{\partial\theta}\right)\right\} \quad (13$$

which comes from the $\hat{\phi}$ term.

In spherical coordinates, equation 4 is

$$\frac{1}{r^2}\frac{\partial}{\partial r}(r^2B_r)+\frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta B_\theta)+\frac{1}{r\sin\theta}\frac{\partial B_\phi}{\partial\phi}=0 \quad (14$$

and is true both inside and outside the material.

Outside the material where there is no magnetic or paramagnetic behavior (or currents for that matter) we have $\vec{M}=0$ so equation 6 becomes $\vec{\nabla}\times\vec{B}=0$ which in spherical coordinates is

$$\frac{\partial}{\partial\theta}(\sin\theta B_\phi)-\frac{\partial B_\theta}{\partial\phi}=0 \quad (15$$

$$\frac{1}{\sin\theta}\frac{\partial B_r}{\partial\phi}-\frac{\partial(\mathrm{rB}_\phi)}{\partial r}=0 \quad (16$$

$$\frac{\partial(\mathrm{rB}_\theta)}{\partial r}-\frac{\partial B_r}{\partial\theta}=0 \quad (17$$

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

$$\vec{B}=B_0\hat{z}=B_0(\cos\theta\hat{r}-\sin\theta\hat{\theta}) \quad (18$$

Note that this satisfies equations 14-17 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

$$B_r|_{r=d/2}=b_r|_{r=d/2} \quad (19$$

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

$$B_t=b_t-\mu_0M_t(b) \quad (20$$

where the subscript t is for tangential. For the specific case of spherical particles we have

$$B_\theta=b_\theta\left(1-\frac{\mu_0M_s}{b}\frac{1-3^{-ab}}{1+3^{-ab}}\right) \quad (21$$

$$B_\phi=b_\phi\left(1-\frac{\mu_0M_s}{b}\frac{1-3^{-ab}}{1+3^{-ab}}\right) \quad (22$$

and the evaluation is at the boundary $r=d/2$, $b=\sqrt{b_r^2+b_\theta^2+b_\phi^2}$. Now, we can simplify a lot because the field in equation 18 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 22, we must also have b_ϕ zero on the boundary, and by extension (from 4 and 14) 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 17 and 14 for the outside field, and 13 and the corresponding inside version of 14 with lower case variables. We can rewrite these equations without the rotational component in the ϕ direction and our problem becomes two dimensional.

From 17 we have

$$B_\theta + r\frac{\partial B_\theta}{\partial r} - \frac{\partial B_r}{\partial \theta} = 0 \qquad (23$$

From 14 we get (for outside variables)

$$\frac{2}{r}B_r + \frac{\partial B_r}{\partial r} + \frac{\cot\theta}{r}B_\theta + \frac{1}{r}\frac{\partial B_\theta}{\partial \theta} = 0 \qquad (24$$

and from 14 for inside variables

$$\frac{2}{r}b_r + \frac{\partial b_r}{\partial r} + \frac{\cot\theta}{r}b_\theta + \frac{1}{r}\frac{\partial b_\theta}{\partial \theta} = 0 \qquad (25$$

and finally the monster equation 13 is

$$\left[\frac{1}{\mu_0} - \frac{M_s}{b}\left(\frac{1-3^{-ab}}{1+3^{-ab}}\right)\right]\left(\frac{b_\theta}{r} + \frac{\partial b_\theta}{\partial r} - \frac{\partial b_r}{\partial \theta}\right) + \qquad (26$$
$$\frac{M_s}{b^2(1+3^{-ab})}\left[\frac{2a\ln 3\, 3^{-ab}}{1+3^{-ab}} - \frac{1-3^{-ab}}{b}\right]\left[b_\theta^2\frac{\partial b_\theta}{\partial r} + b_\theta b_r\left(\frac{\partial b_r}{\partial r} - \frac{1}{r}\frac{\partial b_\theta}{\partial \theta}\right) - \frac{b_r^2}{r}\frac{\partial b_r}{\partial \theta}\right] = 0$$

The next step is to begin to see if there is any kind of analytical solution to these equations. 23 and 24 allow separation of variables, but 26 probably does not. This will be investigated further.

Free space equations

Let's begin by rewriting 23 and 24 in the original form

$$\frac{\partial(\mathrm{rB}_\theta)}{\partial r} = \frac{\partial B_r}{\partial \theta} \qquad (27$$

$$\frac{1}{r}\frac{\partial}{\partial r}(r^2 B_r) = -\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}(\sin\theta\, B_\theta) \qquad (28$$

These two equations will allow separation of variables. We take

$$B_\theta = \mathcal{B}_\theta(r)\mathfrak{B}_\theta(\theta) \qquad (29$$

$$B_r = \mathcal{B}_r(r)\mathfrak{B}_r(\theta) \qquad (30$$

Putting 29 and 30 into 27 and 28 we find after a bit of manipulation

$$\frac{1}{\mathcal{B}_r}\frac{\partial}{\partial r}(r\mathcal{B}_\theta) = \frac{1}{\mathfrak{B}_\theta}\frac{\partial \mathfrak{B}_r}{\partial \theta} \quad (31$$

$$\frac{1}{r\mathcal{B}_\theta}\frac{\partial}{\partial r}\left(r^2\mathcal{B}_r\right) = -\frac{1}{\sin\theta\,\mathfrak{B}_r}\frac{\partial}{\partial \theta}(\sin\theta\,\mathfrak{B}_\theta) \quad (32$$

In both equations 31 and 32 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 31 be equal to the constant β and the terms in equation 32 be equal to the constant γ.

For the radial equations we have

$$\frac{\partial}{\partial r}(r\mathcal{B}_\theta) = \beta\mathcal{B}_r \quad (33$$

$$\frac{\partial}{\partial r}\left(r^2\mathcal{B}_r\right) = \gamma r\mathcal{B}_\theta \quad (34$$

Putting 34 into 33 we find

$$\frac{\partial^2}{\partial r^2}\left(r^2\mathcal{B}_r\right) - \beta\gamma\mathcal{B}_r = 0 \quad (35$$

A transformation of variables with $T = r^2\mathcal{B}_r$ turns 35 into

$$\frac{\partial^2 T}{\partial r^2} - \frac{\beta\gamma}{r^2}T = 0 \quad (36$$

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

$$k(k+1) - \beta\gamma = 0 \quad (37$$

Solving for k we find

$$k = \frac{1 \pm \sqrt{1+4\beta\gamma}}{2} \quad (38$$

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

$$\mathcal{B}_r = \mathrm{Ar}^{\frac{-3+\sqrt{1+4\beta\gamma}}{2}} + Br^{\frac{-3-\sqrt{1+4\beta\gamma}}{2}} \quad (39$$

From equation 34 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

$$\mathcal{B}_\theta = \frac{1}{2\gamma}\left[A\left(1+\sqrt{1+4\beta\gamma}\right)r^{\frac{-3+\sqrt{1+4\beta\gamma}}{2}} + B\left(1-\sqrt{1+4\beta\gamma}\right)r^{\frac{-3-\sqrt{1+4\beta\gamma}}{2}}\right]y \quad (40$$

Equations 39 and 40 are the general radial solutions to any 2D spherical problem of the form described by equations 23 and 24. We now turn our attention to the angular portion of the problem using the same constants β and γ in equations 31 and 32.

From the right hand sides of 31 and 32 we find

$$\frac{\partial \mathfrak{B}_r}{\partial \theta} = \beta\mathfrak{B}_\theta \quad (41$$

$$\frac{\partial}{\partial \theta}(\sin\theta\,\mathfrak{B}_\theta) = -\gamma\sin\theta\,\mathfrak{B}_r \quad (42$$

Putting 41 into 42 we get

$$\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\mathfrak{B}_r}{\partial\theta}\right)=-\,\beta\gamma\sin\theta\,\mathfrak{B}_r \qquad (43$$

We now do the standard change of variables with

$$x=\cos\theta \qquad (44$$

so that $\frac{\partial}{\partial\theta}=-\sin\theta\frac{\partial}{\partial x}$ which transforms equation 43 into the form

$$\frac{\partial}{\partial x}\left((1-x^2)\frac{\partial}{\partial x}\mathfrak{B}_r\right)+\beta\gamma\,\mathfrak{B}_r=0 \qquad (45$$

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

$$\beta\gamma=\nu(\nu+1) \qquad (46$$

and the solution to 45 is given by

$$\mathfrak{B}_r=CP_\nu(\cos\theta)+DQ_\nu(\cos\theta) \qquad (47$$

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

$$(x^2-1)\frac{d}{dx}P_\nu(x)=(\nu+1)[P_{\nu+1}(x)-xP_\nu(x)] \qquad (48$$

$$(x^2-1)\frac{d}{dx}Q_\nu(x)=(\nu+1)[Q_{\nu+1}(x)-xQ_\nu(x)] \qquad (49$$

From the transformations $\frac{\partial}{\partial\theta}=-\sin\theta\frac{\partial}{\partial x}$ and $-\sin^2\theta=x^2-1$ we can convert equation 41 into

$$\sin\theta\frac{\partial\mathfrak{B}_r}{\partial\theta}=(x^2-1)\frac{\partial\mathfrak{B}_r}{\partial x}=\beta\sin\theta\,\mathfrak{B}_\theta \qquad (50$$

With formulas 47, 48 and 49 we can solve for $\mathfrak{B}_\theta$ in 50. This gives

$$\mathfrak{B}_\theta=\frac{1}{\beta}\frac{\partial\mathfrak{B}_r}{\partial\theta}=\frac{\nu+1}{\beta\sin\theta}[CP_{\nu+1}(\cos\theta)+DQ_{\nu+1}(\cos\theta)-\cos\theta(CP_\nu(\cos\theta)+DQ_\nu(\cos\theta))] \qquad (51$$

We can now combine equations 39 and 47 to get the solution for B_r and equations 40 and 51 for B_θ. We substitute $\beta\gamma=\nu(\nu+1)$ in all these equations and get the final result

$$B_r(r,\theta)=\left(\mathrm{A}r^{\frac{-3+\sqrt{1+4\nu(\nu+1)}}{2}}+Br^{\frac{-3-\sqrt{1+4\nu(\nu+1)}}{2}}\right)(CP_\nu(\cos\theta)+DQ_\nu(\cos\theta)) \qquad (52$$

$$B_\theta(r,\theta)=\frac{1}{2\nu\sin\theta}\left[A\left(1+\sqrt{1+4\nu(\nu+1)}\right)r^{\frac{-3+\sqrt{1+4\nu(\nu+1)}}{2}}+B\left(1-\sqrt{1+4\nu(\nu+1)}\right)r^{\frac{-3-\sqrt{1+4\nu(\nu+1)}}{2}}\right][C\,P_{\nu+1}(\cos\theta)+D\,Q_{\nu+1}(\cos\theta)-\cos\theta(C\,P_\nu(\cos\theta)+DQ_\nu(\cos\theta))] \qquad (53$$

Far field conditions

Equation 18 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

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

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

It's really obvious that the Q's don't work in the limit for large r, so D must be zero. From equation 18 we see that

$$B_r = B_o\cos\theta \qquad (54$$

can be satisfied exactly if $\nu = 1$ because equation 52 becomes

$$B_r = \left(A + \frac{B}{r^3}\right)\cos\theta \qquad (55$$

in the limit $r \to \infty$ 55 reduces to 54 and $A = B_0$. This fixes the solution for B_θ to be (from equation 53)

$$B_\theta = \frac{1}{2\sin\theta}\left[4B_0 - 2\frac{B}{r^3}\right]\left[\frac{1}{2}(3\cos^2\theta - 1) - \cos^2\theta\right] \qquad (56$$

With a little algebra we find that this reduces to

$$B_\theta = -\sin\theta\left(B_0 - \frac{B}{2r^3}\right) \qquad (57$$

Which is exactly what we need to meet the $r \to \infty$ conditions of the boundary condition from equation 18.

Near field equations

Because the free space has no material, it was possible to find exact solutions to the equations describing the magnetic field. In equation 26 we have terms with

$$3^{-ab} \qquad (58$$

where

$$b = \sqrt{b_r^2 + b_\theta^2} \qquad (59$$

To even begin having a hope of analytically solving equation 26 we would first guess b is a constant. This gives us the free space equations back, and we are left with equations of the form 54 and 57. That this is true can be seen by looking at equations 3 and 10. The second line of equation 26 comes from 10, which is the gradient of the equation 59 squared. If equation 59 describes a constant, then it's gradient is zero. This returns us to the free space equations.

Unfortunatly, pursuit of this guess leads us to the value of $b = 0$ as the only constant which satisfies some of the formulas, but this gives division by 0 in the boundary conditions. Only a numerical solution is possible. This will be pursued as the next step in the problem.

As a first step toward a numerical solution, I begin with a transformation of variables to dimensionless parameters. The very small numbers of actual dimensions are then changed into values in the range of unity which keeps the computer representation of numbers reasonable. The obvious choice for r is the radius of the particle, but we normally deal with the diameter of these tiny particles so let's take

$$s = \frac{r}{d} \qquad (60$$

Since $a = \frac{1}{B_{1/2}}$ is a measure of inverse magnetic field strength, I take

$$\beta = \sqrt{\beta_s^2 + \beta_\theta^2} \qquad (61$$

where $\beta = ab$, $\beta_s = ab_r$ and $\beta_\theta = ab_\theta$. Clearing denominators of all possible division by zero values also helps computer calculations as does fully expanding all derivatives. The final dimensionless parameter to introduce will appear by multiplying through by μ_0

$$m = \mu_0 M_s a \qquad (62$$

Equations 26 and 25 then become

$$\left[\beta^2 - m\beta\left(\frac{1-3^{-\beta}}{1+3^{-\beta}}\right)\right]\left(\beta_\theta + s\frac{\partial\beta_\theta}{\partial s} - \frac{\partial\beta_s}{\partial\theta}\right) + \frac{m}{1+3^{-\beta}}\left(\frac{2\ln 3 3^{-\beta}}{1+3^{-\beta}} - \frac{1-3^{-\beta}}{\beta}\right)\left[s\beta_\theta^2\frac{\partial\beta_\theta}{\partial s} - \beta_r^2\frac{\partial\beta_s}{\partial\theta} + \beta_\theta\beta_r\left(s\frac{\partial\beta_s}{\partial s} - \frac{\partial\beta_\theta}{\partial\theta}\right)\right] = 0 \qquad (63$$

$$\sin\theta\,\beta_s + s\sin\theta\,\frac{\partial\beta_s}{\partial s} + \cos\theta\,\beta_\theta + \sin\theta\,\frac{\partial\beta_\theta}{\partial\theta} = 0 \qquad (64$$

In addition, we have the boundary conditions specified by equations 19 and 21. Let

$$\delta_0 = aB_0 \qquad (65$$

and combine 19 and 21 with 55 and 57 to get

$$\beta_{s_{s=1/2}} = \delta_0\left(1 + \frac{c}{d^3}\right)\cos\theta \qquad (66$$

$$\beta_\theta\left(1 - \frac{m}{\beta}\frac{1-3^{-\beta}}{1+3^{-\beta}}\right)_{s=1/2} = -\,\delta_0\left(1 - \frac{c}{2d^3}\right)\sin\theta \qquad (67$$

where c is an unknown constant. We can eliminate c to find a relationship between the maximum external field, β_s and β_θ for every point on the surface (i.e. as a function of θ). For convienience let

$$\delta_\theta = \beta_{\theta\, s=1/2} \qquad (68$$

and

$$\delta_s = \beta_{s\, s=1/2} \qquad (69$$

with

$$\delta = \sqrt{\delta_s^2 + \delta_\theta^2} \qquad (70$$

By looking hard at equations 66 and 67 we note that the functions δ_s and δ_θ will be easier to deal with if we assume (and this is a major assumption here) that they have the form

$$\delta_s = K\cos\theta \quad (71$$

$$\delta_\theta = -K\sin\theta \quad (72$$

Then δ in equation 70 becomes

$$\delta = \sqrt{K^2\cos^2\theta + K^2\sin^2\theta} = |K| \quad (73$$

Unfortunatly, the absolute value in 67 runs us into a lot of trouble. To mitigate these problems, we make a further assumption, which allows us to eliminate the trouble and more easily solve the problem. Moving K onto the complex plane allows us to deal with the absolute value in a much simpler way - it is the radius of a circle about the origin. The plus and minus values for K in 71 and 72 are then found at the angles of 0 and π in the complex plane. Thus we take

$$K = \kappa e^{i\psi} \quad (74$$

Combining 66, 67, 71, 72 and 74 we get

$$\kappa e^{i\psi} = \delta_0\left(1 + \frac{c}{d^3}\right) \quad (75$$

$$\kappa e^{i\psi}\left(1 - \frac{m}{\kappa}\frac{1-3^{-\kappa}}{1+3^{-\kappa}}\right) = \delta_0\left(1 - \frac{c}{2d^3}\right) \quad (76$$

From 75 we can find

$$\frac{c}{d^3} = 1 - \frac{\kappa}{\delta_0}e^{i\psi} \quad (77$$

which we can put into 76 and rearrange terms to find

$$\frac{3}{2}\kappa - m\frac{1-3^{-\kappa}}{1+3^{-\kappa}} = \frac{3}{2}\delta_0 e^{-i\psi} \quad (78$$

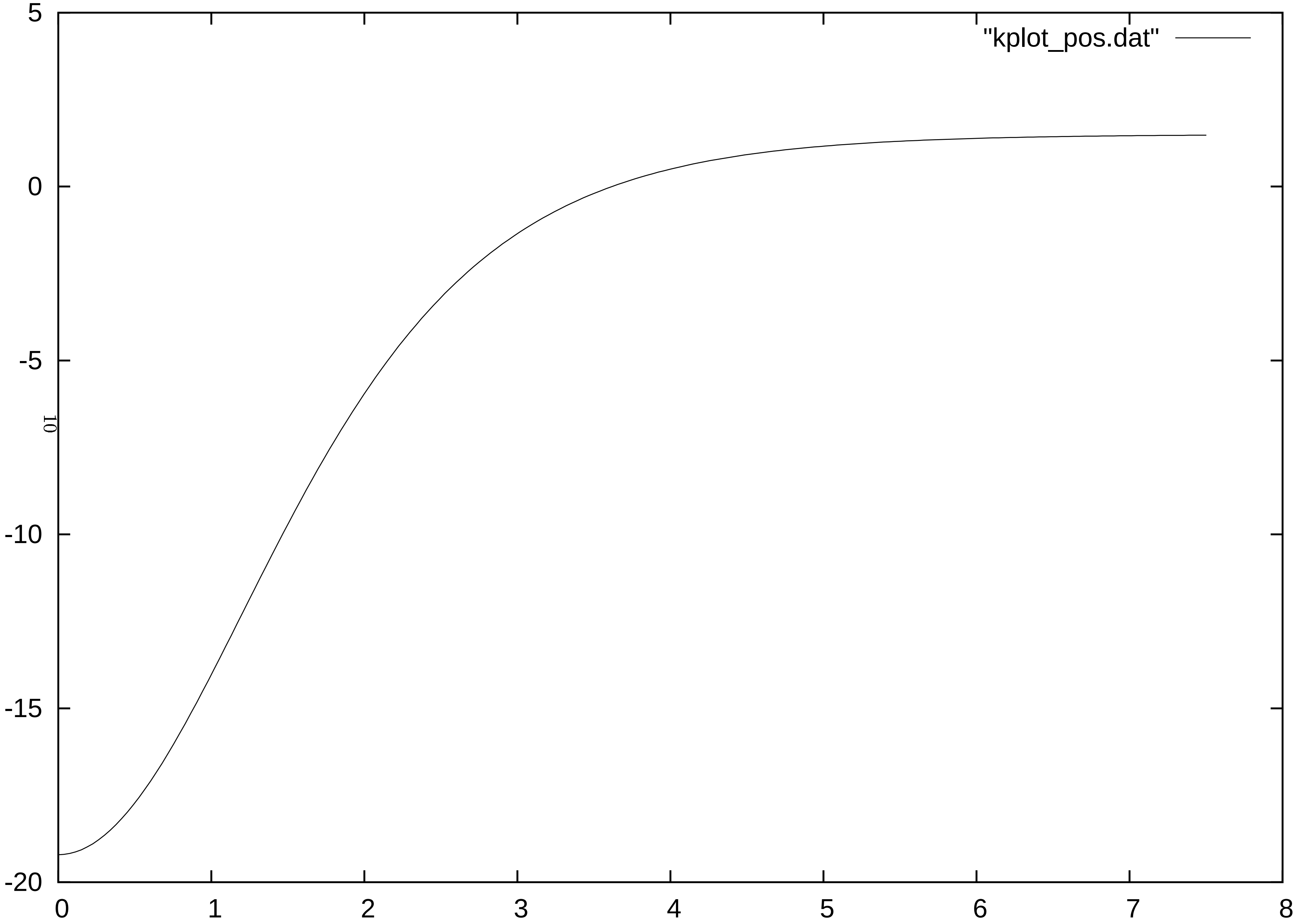
For our purposes, only $\psi = 0$ and $\psi = \pi$ are of interest. Other values might lead to interesting insights into the problem. Numerically it is easier to deal with equation 78 in a different form. Multiply the second term on the left by 3^κ on top and bottom to get

$$f(\kappa) = \frac{3}{2}\kappa - m\frac{3^\kappa - 1}{3^\kappa + 1} - \frac{3}{2}\delta_0 e^{-i\psi} = 0 \quad (79$$

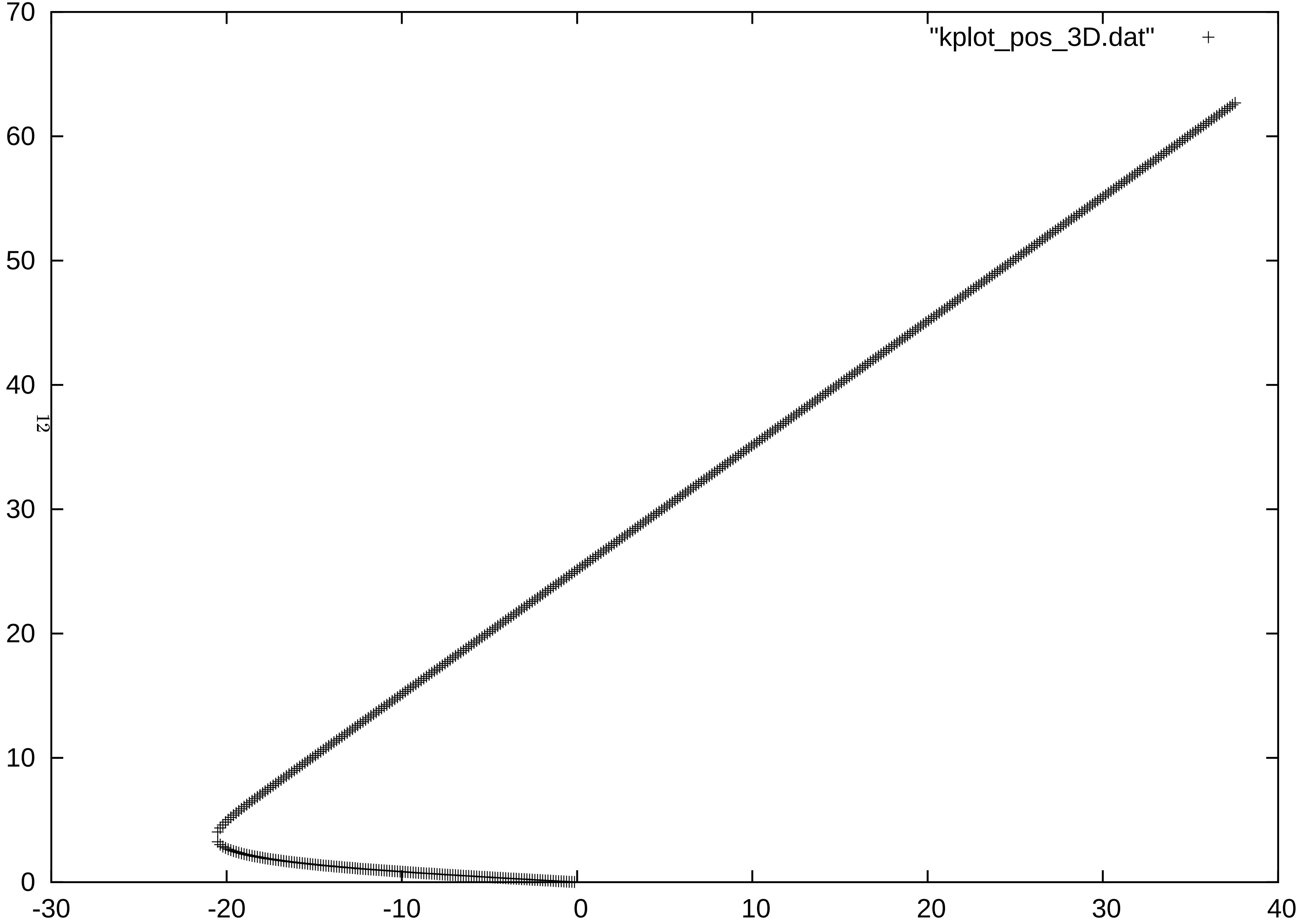
Taking the derivative of equation 79 with respect to κ gives us an idea on how to proceed in finding values for κ when the right hand side of 79 is not zero (by inspection $\kappa = 0$ is a solution). The derivative is

$$f'(\kappa) = \frac{3}{2} - m\frac{2\ln 3\, 3^\kappa}{(3^\kappa + 1)^2} \quad (80$$

The following figure is a plot of equation 80 over the range of 0 to 8 in κ for $m = 37.70$. The horizontal axis is δ_0, the vertical axis is $f'(\kappa)$.


"kplot_pos.dat"
5
0
-5
-10
-15
-20
10
0
1
2
3
4
5
6
7
8

The zero crossing occurs near $\kappa = 3.6$ and we can use this see that there could be two solutions to equation 79. A 3 dimensional plot of 79 shows that each curve along δ_0 from large negative to large positive is similar, and since equation 80 is independent of δ_0 this makes sense. However, below a certain negative value, there are no solutions possible. I wrote code to find the zero crossings in equation 79 using all this information. Letting $\pm\,\delta_0$ replace $e^{i\psi}$ I found the following plot of values. The horizontal axis is δ_0, the vertical axis is κ, and all values were computed with $m = 37.70$, for magnetite.


"kplot_pos_3D.dat"
0
10
20
30
40
50
60
70
-30
-20
-10
0
10
20
30
40

In terms of K with δ_0 always positive the above plot becomes quite strange. The negative portion of δ_0 becomes the negative portion of K so it folds over from the second quadrant down into the 4th quadrant. This means there are 3 possible values for K at a given δ_0. That says the boundary conditions can give rise to 3 possible configurations of field inside the magnetite.

So in spite of the fact that the material behaves as superparamagnetic, there can be a large residual field inside the particle once it has been expose to a high field. This may or may not be a physical solution - but in any event shows that strange behavior can be expected in ferrofluids when the field strength is low, and history of the particle is taken into account.

The next step is to find the full field solutions inside the magnetite using the above solutions for the constants in equation 77. The constant c has dimensions of volume, so we can think of this as the ratio of effective radius. Let

$$\frac{c}{d^3} = \left(\frac{\rho}{d}\right)^3 \qquad (81$$

When r (or s) gets larger than the effective radius, the external field loses the influence from the particle. But as we can see from the equations, the effective radius grows with external field. So stronger fields will produce more interaction between particles. But the interaction is complex since the fields can flip over and the particle can act antiferromagneticly. As I said, this may not be a real physical solution, but it certainly is an interesting possiblility to check experimentally.

Appendix 1

The following was an attempt at solving the boundary conditions on the surface of the magnetite. This is not really useful because the variables are not actually solved - and the choices for real solutions are not clear. However, the plots from the resulting equations are still interesting.

Putting 68 - 70 into 66 and 67, then multiply 66 by sinθ and 67 by cosθ and subtract 66 from 67 I get

$$\delta_\theta \cos\theta \left(1 - \frac{m}{\delta} \frac{1 - 3^{-\delta}}{1 + 3^{-\delta}}\right) - \delta_s \sin\theta = -2\delta_0 \sin\theta \cos\theta \qquad (A-1$$

Equations 63, 64 and A-1 are all that are required to find the field inside the particle. The external field will match the boundary conditions 66 and 67 correctly, assuming we can find solutions to 63 and 64 which satisify equation A-1. This reduces the numerical analysis substantially because we only need to find the solution to field inside the sphere.

The main reason we can do this comes from the fact that we're only doing a 2D problem and because the external field is simple. To get a feel for how equation 71 behaves, I plot it for several values of δ_0 below.

In the following plots, δ_θ is on the vertical axis, θ ranges from 0 to 3 on the x axis and δ_s ranges from -50 to +50 on the y axis. I have used values for M_s as 4.5×10^5A/m and $B_{1/2} = 0.015$ so that $m = 37.70$ is a constant. In figure 1 I have $\delta_0 = m$, in figure 2 $\delta_0 = m/2$, and in figure 3 $\delta_0 = m/2 - 1$. For higher and lower values of δ_0 the plots do not change very much. The "S" curve function in equation 2 is the driving force behind this. Figure 4 shows $\delta_0 = 5.0$.

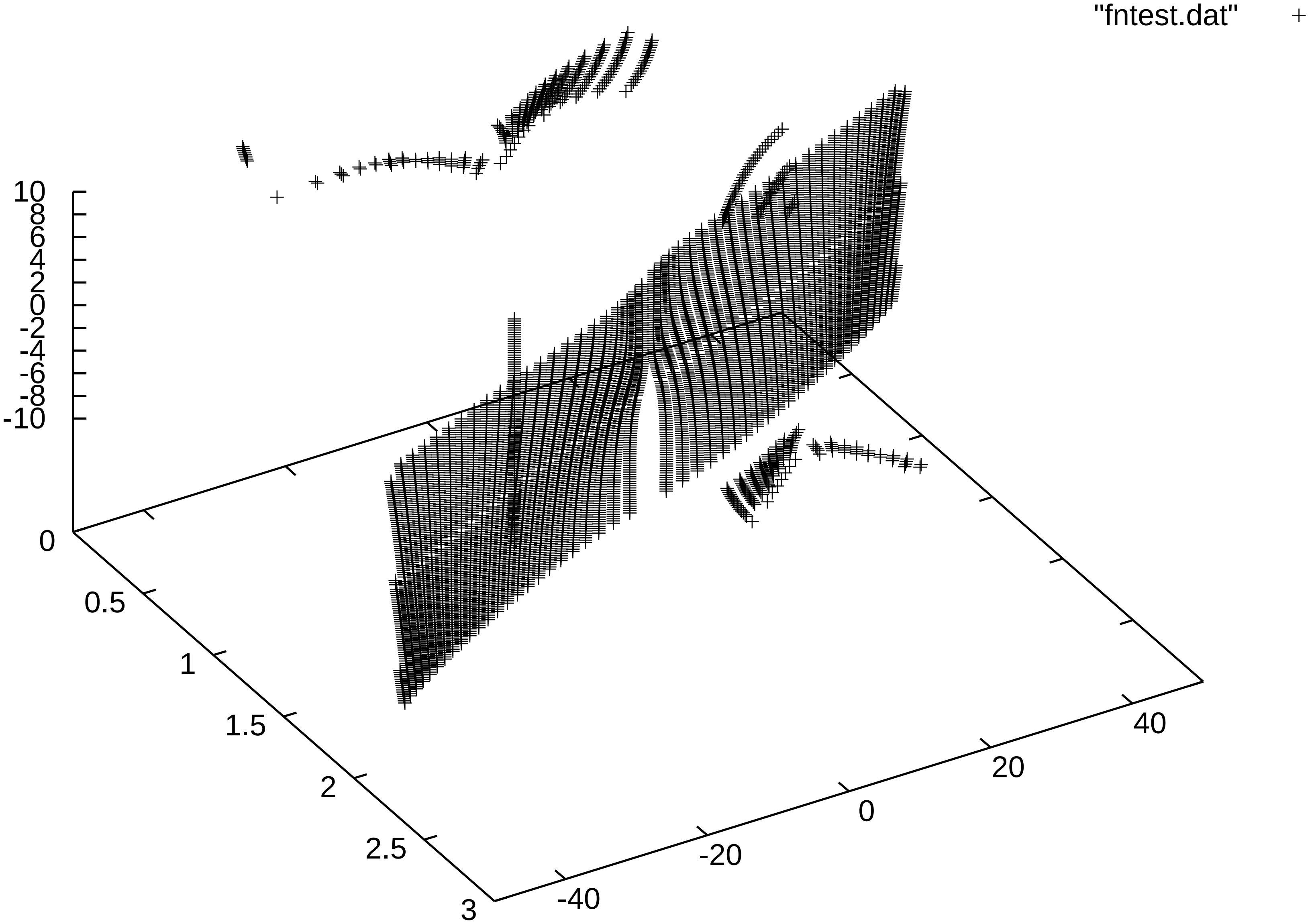

"fntest.dat"
10
8
6
4
2
0
-2
-4
-6
-8
-10
0
0.5
1
1.5
2
2.5
3
-40
-20
0
20
40

Figure 1: $\delta_0 = m$ is ploted for equation A-1.

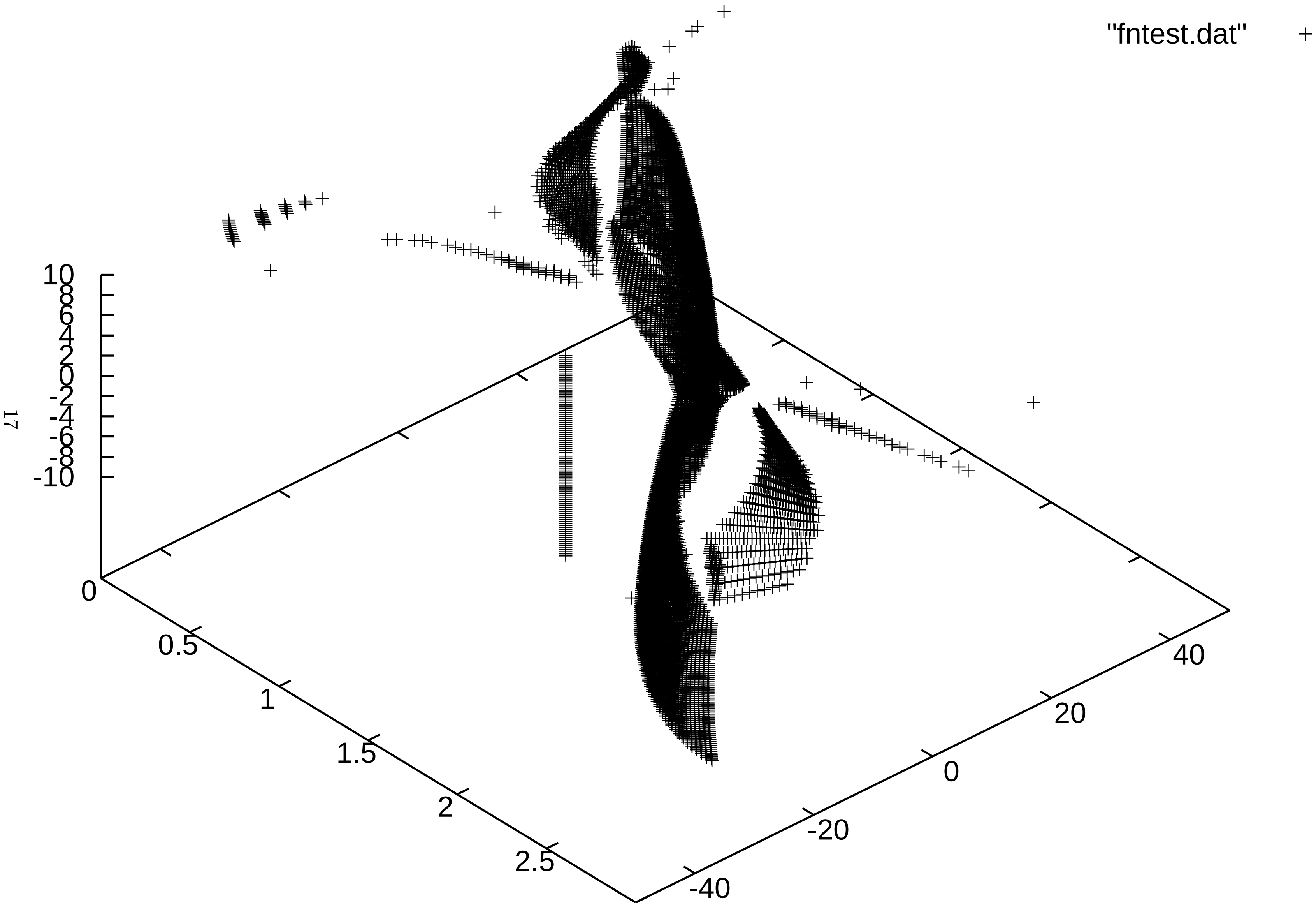

"fntest.dat"
10
8
6
4
2
0
-2
-4
-6
-8
-10
0
0.5
1
1.5
2
2.5
-40
-20
0
20
40

Figure 2: $\delta_0 = \frac{m}{2}$ for equation A-1.

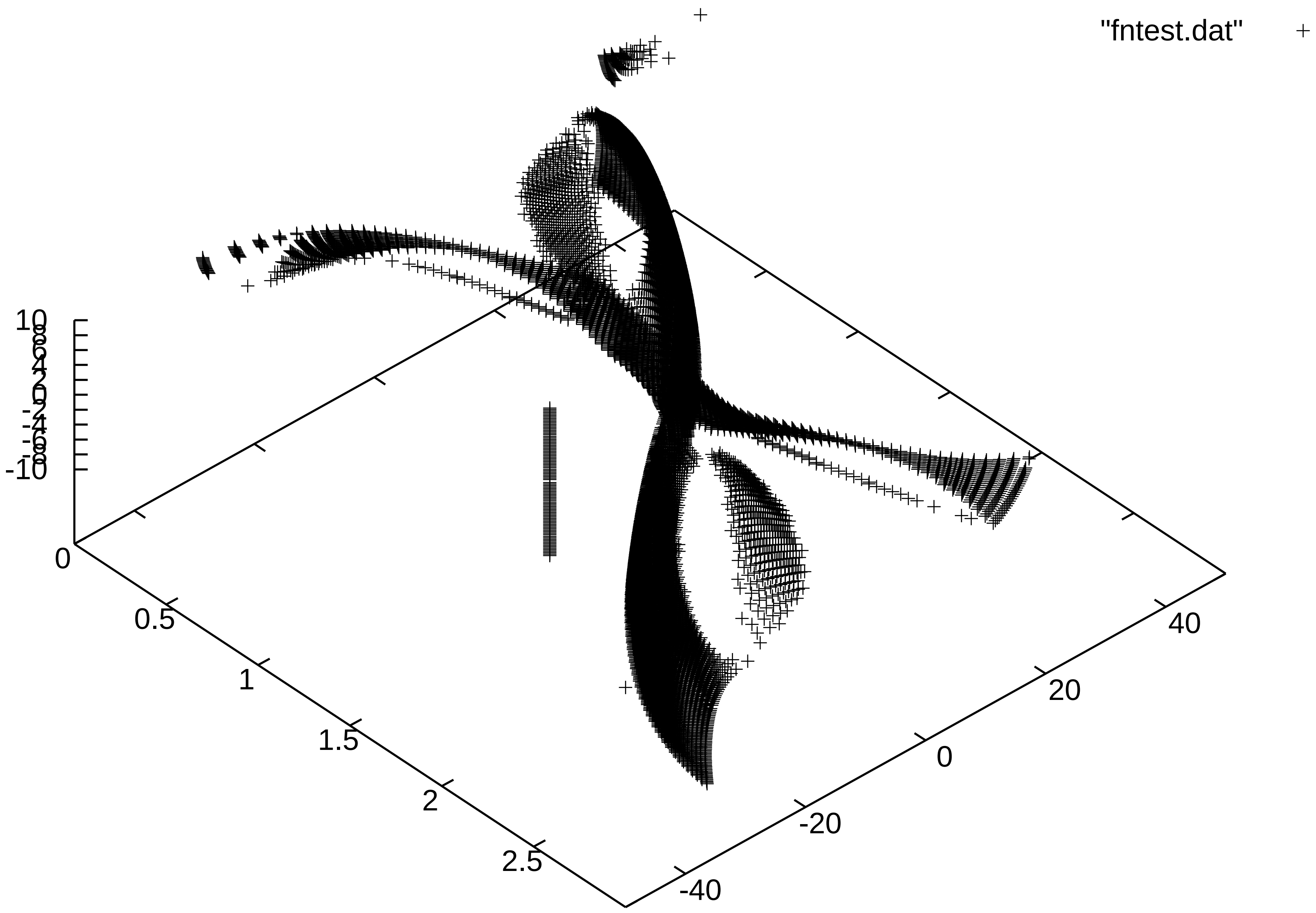

"fntest.dat"
10
-10
0
0.5
1
1.5
2
2.5
-40
-20
0
20
40

Figure 3: $\delta_0 = \frac{m}{2} - 1$ for equation A-1.

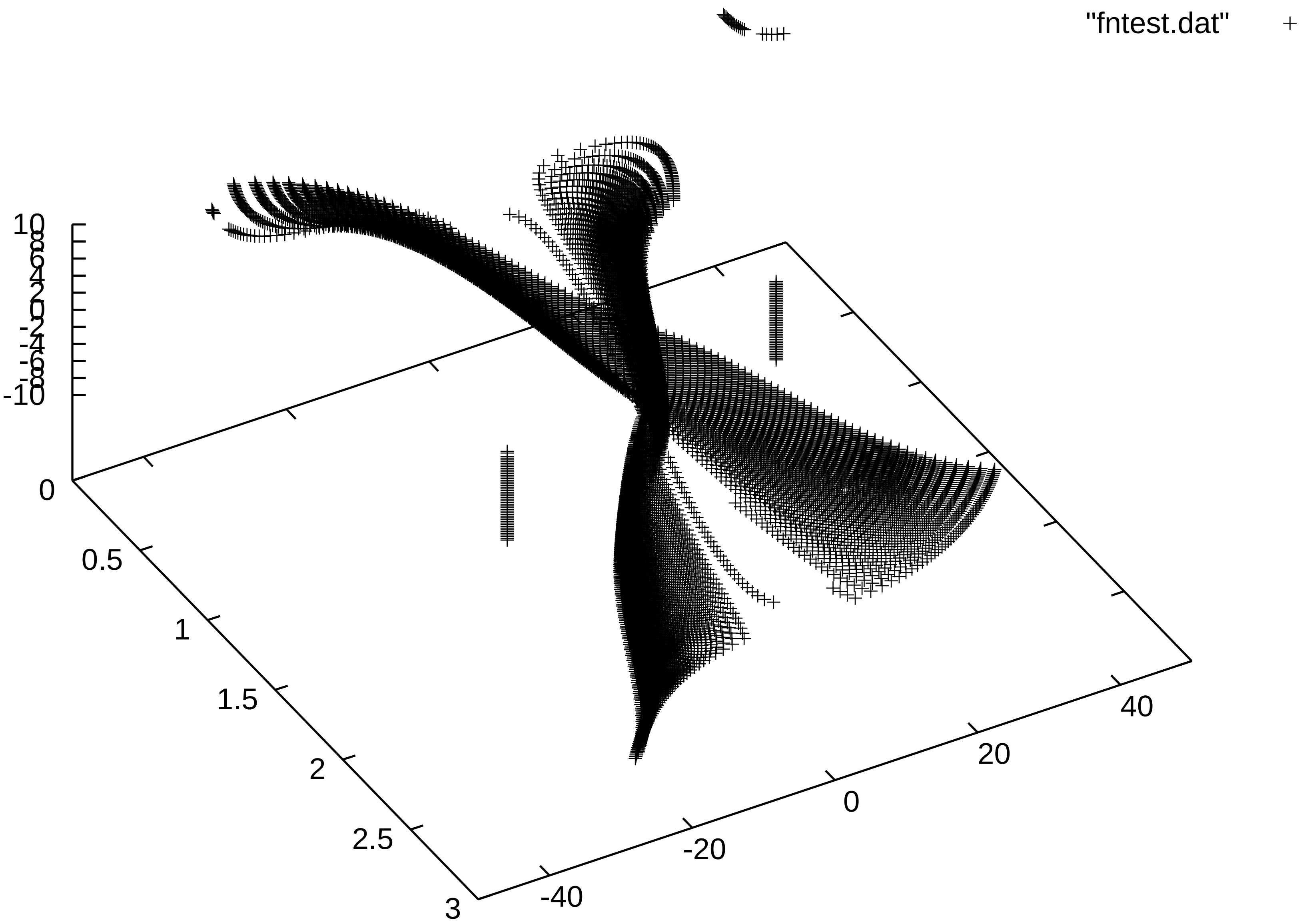

"fntest.dat"
10
8
6
4
2
0
-2
-4
-6
-8
-10
0
0.5
1
1.5
2
2.5
3
-40
-20
0
20
40

Figure 4: $\delta_0 = 5.0$ in equation A-1.

The above figures were plotted using Newton's method as a root finding operation. The plots were made by sweeping across values of θ in steps of $\pi/100$ and values of δ_θ in the range -10 to + 10 in steps of 0.1. The choice of where to look for the root may be the cause for several strange looking chunks of data in the plots. There may be more than one solution for δ_s to equation A-1 for a particular choice of δ_θ. Figure 5 below shows a larger range of δ_θ between -50 and +50 for the same plot as figure 1.

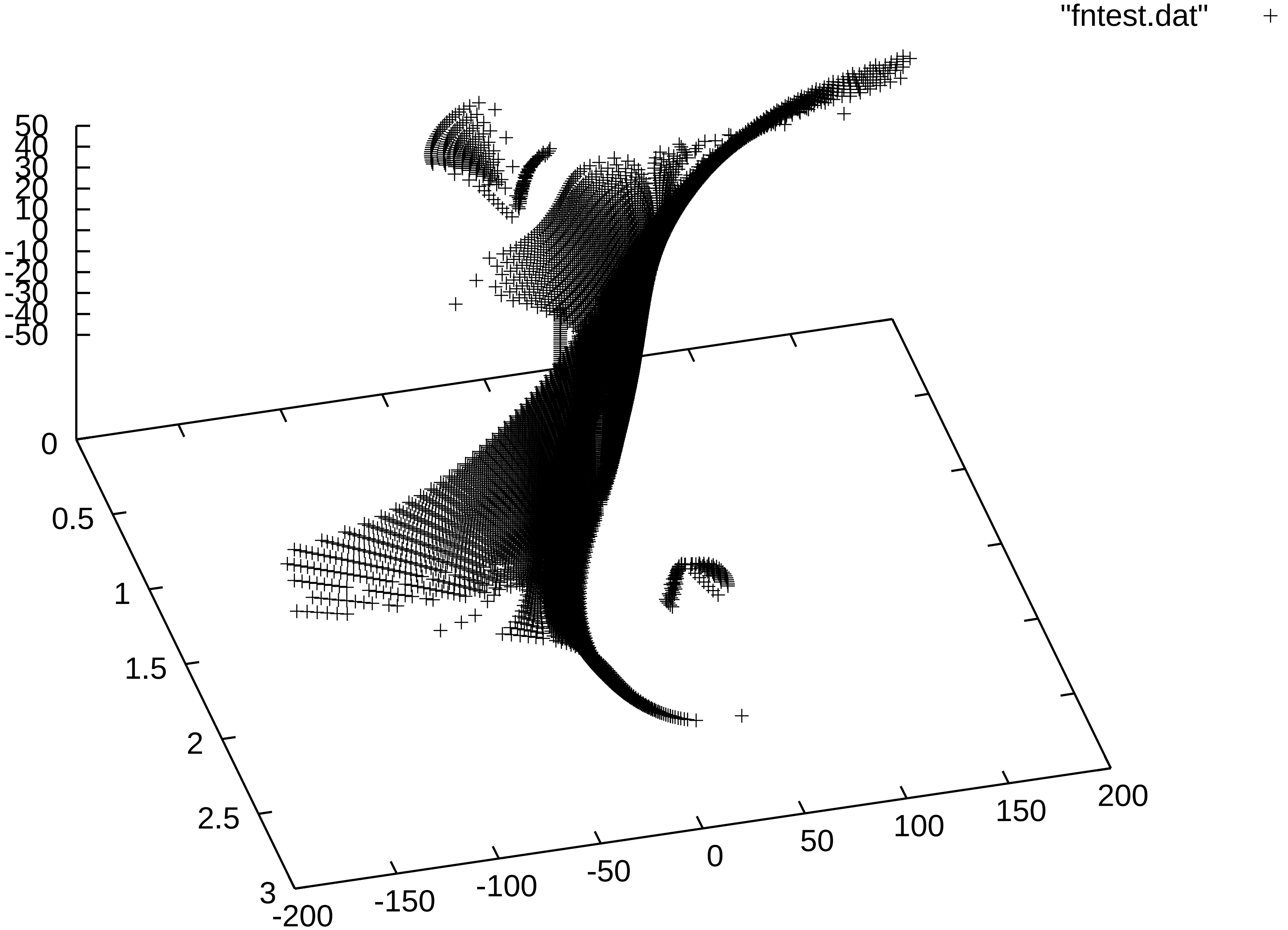

"fntest.dat"
50
40
30
20
10
0
-10
-20
-30
-40
-50
0
0.5
1
1.5
2
2.5
3
-200
-150
-100
-50
0
50
100
150
200

Figure 5: Same as figure 1 but over larger range in δ_θ.

It is really difficult to see the swooping surface that equation A-1 elicits without moving the graph in 3D. Needless to say, we'll need to be careful while solving the numerical problem of the differential equations!