



Department of Physics and Astronomy
2nd Year Laboratory

G4 Quinckes method

Scientific aims and objectives

- To determine the *volume* magnetic susceptibility of two different concentration solutions of Manganese ions.
- To compare the values determined from the two solutions in the context of experimental errors *and* assumptions made in the Quincke's method equations
- To compare your experimentally determined value of magnetic susceptibility with the theoretical value, using the quantum of magnetic moment, the Bohr magneton.

Learning Outcomes

- To know how to apply a calibration function.
- To use repeat measurements to determine uncertainty.
- To apply a polynomial fitting function using an excel plugin
- To use molar quantities in calculations.
- To understand that many scientific equations are derived using approximations,

Apparatus

- Electromagnet and power supply
- Hall probe for B field measurement.
- Solutions of Manganese sulphate $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$: 75 mg/100ml; 25 mg/100ml
- *Specific gravity* weighting bottle, balance, De-ionised water, compressed air gun for drying the U-tube.
- U-tube, micrometer, measuring stick
- "PolyFit" Excel plug-in software
- χ^2 Excel software

Safety instructions

- Never leave the magnet running at high current (>5 A) for extended periods of time (>5 minutes)
- Take care when carrying the U-tube between cleaning and experimental stations
- Wear gloves and safety goggles when dispensing $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ solutions.

Task 1 - Pre-session questions

You are required to complete the questions found at the back of the script before starting your laboratory work. These questions will prepare you for the experiment by teaching you how to install and use "PolyFit" software to fit a higher order polynomial function to experimental data, to understand the use of a calibration function and to introduce you to the quantum description of magnetism.

Task 2 – The experiment

The objective is to measure the magnetic susceptibility (per unit volume, i.e. per m³) of two different concentration solutions of MnSO₄·4H₂O. This can be done by measuring the equilibrium displacement of the solution of Mn²⁺ ions as acted on by a net magnetic force due to an external magnetic field and the weight of the solution due to gravity.

The diagram illustrates the experimental setup for measuring magnetic susceptibility. A U-tube is placed between the North (N) and South (S) poles of a magnet, creating a magnetic field B_z . The liquid level in the left arm is displaced by a height h relative to the right arm. A balance scale is shown with two bottles: one containing 75 g/100ml and the other 25 g/100ml of MnSO₄·4H₂O solution. The formula for magnetic susceptibility is given as $\chi_{Mn} = \frac{Np^2\mu_B^2\mu_0}{3kT}$. Below the bottles, the equation $(\chi - \chi_a)(B^2 - B_0^2) = 4\mu_0 h(\rho - \rho_a)g$ is shown. To the right, a table shows the electron configuration for Mn²⁺ with 5 unpaired electrons.

Mn ²⁺		$p = g\sqrt{J(J+1)} = 5.92$	
s	p	d	
1	↑↓		$J=L+S$
2	↑↓	↑↓ ↑↓ ↑↓	$S = 5/2 \quad L=0$
3	↑↓	↑↓ ↑↓ ↑↓	
4		↑ ↑ ↑ ↑	

You will need to calibrate the magnetic field using a Hall probe and determine the error associated with the calibration function you generate. You will also need to measure the density of the Mn²⁺ solutions and calculate the number of moles of Mn²⁺ present in the solution. You should consider the error in these calculations. Mn²⁺ is a paramagnetic material with 5 unpaired electrons giving rise to a significant magnetic moment. You can use the quantum theory of magnetic moments of atoms to compare your experimentally determined values. The two different concentration solutions *should* give you the same value for the magnetic moment of Mn²⁺, but due to experimental error, and assumptions made when deriving the relationship between volume magnetic susceptibility and ionic magnetic moments of the solutions, they will actually yield different values. You should endeavour to understand the origin of these differences by carefully numerating the errors present in the experiment and understanding the assumptions made in the derivation of the Quincke equation. χ^2 should be used when fitting a straight line to the experimental data. The best way to determine experimental errors required by χ^2 is to make repeat measurements and take a mean and standard deviation.

Task 3 – Reporting

You should report the *volume magnetic susceptibility* for the two different solutions as well as two values for the magnetic moment of Mn²⁺ in number of Bohr magnetons. You should attribute uncertainty to all these numbers and discuss the differences in terms of experimental precision and theoretical assumptions made. You should concisely report your working for calculations of number of moles, density and magnetic moment. You should present all your experimental data: calibration and measurement data for the two solutions.

Appendix of supporting information

Contents

1. The magnetic properties of atoms and ions
2. Determination of density and molar concentration
3. Quincke's experimental method
4. Measuring magnetic field with a Hall probe
5. Using PolyFit – A polynomial fitting plug-in for Excel

1. The Magnetic moment of atoms

Ions such as manganese Mn^{2+} possess a permanent magnetic dipole moment due to unpaired 3d electrons. The magnetic dipoles are isotropic within a liquid or amorphous solid. The bulk magnetisation of a material is defined as M , the magnetic dipole moment *per unit volume*. For a paramagnetic material such as Mn^{2+} , the magnetisation M is induced by the applied field B and M is parallel to B .

$$M = (\mu_r - 1) \frac{B}{\mu_0} = \frac{\chi B}{\mu_0} \quad (\text{A1})$$

The volume magnetic susceptibility is defined by the relations,

$$\mu_r = 1 + \chi, \quad \text{where } \chi = M / H \quad (\text{A2})$$

and where the magnetic intensity H is related to B through $B = \mu_0 \mu_r H$.

In this description of the relationship between applied field and magnetisation it is assumed that the magnetic dipoles of neighbouring ions do not interact, a condition that is fulfilled for low concentrations of ions in solution, but not for high concentrations of ions such as those found in a solid. For the non-interacting dipoles and at high temperatures, i.e. where $kT \gg mB$, where m is the magnetisation of a single ion, the contribution to the volume susceptibility χ from the paramagnetic Mn^{2+} ions is given by:

$$\chi_{\text{Mn}} = \frac{\mu_0 M}{B} = \frac{Nm^2 \mu_0}{3kT} = \frac{Np^2 \mu_B^2 \mu_0}{3kT} \quad (\text{A3})$$

where k is Boltzmann's constant and N is the number of Mn ions per unit volume and $m = p\mu_B$, where p is the magneton number of the Mn^{2+} ion, and μ_B is the Bohr magneton, the atomic unit of magnetic moment defined by $\mu_B = \frac{eh}{4\pi m_e}$. The

magnetisation of a single Mn^{2+} ion, m , is calculated from the total angular momentum of an atom or ion, with contributions from both the orbital motion L and the spin of the electrons S . p can be calculated from L and S . These quantum numbers must be determined in the manner consistent with the Pauli exclusion principle that states no *one* specific quantum state can contain more than *one* electron. The quantum numbers for the individual constituent electrons are denoted by letters n , l , m_l , and m_s . n is the principal quantum number and takes values 1, 2, 3, 4 etc.. and is responsible for the defining the period in which the atom lies in the periodic table. l is

the orbital quantum number and can take values up to $n-l$ and defines the shell within the particular period. The different shells are given names s, p, d, f etc.. so the period specific shells take names such as 1s, 2p, 2s, 2p, 3s, 3p, 3d, etc.. The spin of the electron also has a quantum number, m_s , that can take values of $+\frac{1}{2}$ or $-\frac{1}{2}$. The total number of electrons that can occupy an orbital is determined by calculating a final quantum number m_l that defines the sub-shell (leading to the groups in the periodic table). Only two electrons (with opposing spin) can occupy a sub-shell and m_l may take values from $-l, -l+1, -l+2 \dots 0 \dots l-1, l$. So an s orbital with quantum number $l=1$ will have only one value of m_l that can accept only 2 electrons, one with $m_s = +\frac{1}{2}$ and one with $m_s = -\frac{1}{2}$. However a d orbital with $l=3$ can have 5 values of m_l ($-2, -1, 0, 1, 2$), five sub-orbitals, and therefore a total of 10 electrons; two values of m_s for each sub-orbital. Although these rules appear arbitrary and empirical they are a direct result of the quantum mechanical solution of the atom.

The total spin quantum number S can be calculated by adding up the spin of the contributing electrons, either $+\frac{1}{2}$ or $-\frac{1}{2}$. $S = \sum m_s$

The total angular momentum L can be calculated by summing the contributions from the different occupied orbitals. Since the total sub-shell quantum number M_L is the sum of m_l for the contributing electrons, $\sum m_l = M_L$ and M_L takes values $-L, -L+1, \dots 0 \dots L-1, L$ then L is simply the maximum value of M_L . note that only partly filled orbitals contribute to L since $\sum m_l = 0$ for a filled orbital.

The total quantum angular momentum quantum number, J , of an atom or ion can then be calculated by adding the contributions and using the empirical rules that $J = L - S$ if the orbital is less than half filled and $J = L + S$ if the orbital is more than half filled. Finally the magneton number p is given by $p = g\sqrt{J(J+1)}$ where g is the

Landé splitting factor $g = \left\{ \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \right\}$ and takes into account that the spin

effectively creates twice as much magnetic moment as the orbital motion. The S, L, J and p values for some transition metal ions, including, importantly for this experiment Mn^{2+} are given below.

No of electrons in 3d shell	Ion	S	M_L	L	J	p	
0	Ca^{2+}	0	0	0	0	0	
1	Sc^{2+}	$1/2$	-2	2	$3/2$	1.55	
2	Ti^{2+}	1	-3	3	2	1.63	
3	V^{2+}	$3/2$	-3	3	$3/2$	0.77	
4	Cr^{2+}	2	-2	2	0	0	
5	Mn^{2+}	$5/2$	0	0	$5/2$	5.92	
6	Fe^{2+}	2	2	2	4	6.71	
7	Co^{2+}	$3/2$	3	3	$9/2$	6.63	
8	Ni^{2+}	1	3	3	4	5.59	
9	Cu^{2+}	$1/2$	2	2	$5/2$	3.55	
10	Zn^{2+}	0	0	0	0	0	

Diagram illustrating the filling of orbitals for s, p, and d subshells:

- s** ($l=0$): 1 orbital, filled with 2 electrons (up and down arrows).
- p** ($l=1$): 3 orbitals, filled with 6 electrons (up and down arrows in each).
- d** ($l=2$): 5 orbitals, filled with 10 electrons (up and down arrows in each).

For $n=1$ to $n=4$, the orbitals are shown as boxes. The diagram also shows the calculation of J and S :

$J = L + S$ (for more than half filled)

$S = \sum m_s$, $M_L = \sum m_l$

Values for m_l and m_s are shown below the orbitals:

m_l : -2, -1, 0, 1, 2

m_s : $+\frac{1}{2}$, $-\frac{1}{2}$

2. Determination of density and molar concentration

Since you will be determining a *volume susceptibility* and are required to determine the number of Manganese ions per unit volume, N . Therefore you will need to calculate the number of ions per unit volume (per m³) for the two solutions. You are given the concentration of the solutions in mass per volume and the best thing to do is convert this into a number of moles per unit volume for the MnSO₄·4H₂O salt. The dissolved salt already has water incorporated in its structure and this water must be included in the moles calculation as a contribution to the relative molar mass (*RMM*).

You can use the standard conversion equations, $moles = \frac{mass}{RMM}$ and the number of molecules (or ions) $N = moles \times N_A$.

You will also need to determine the density of the two Manganese ion solutions. This can be done using a specific gravity bottle, a special bottle with a hole in its top that enables a precise volume of liquid to be weighed. You should determine the density of the Manganese ion solutions by the mass of the solution with ions and the mass of de-ionised water such that

$$\rho_{MnSO_4 \text{ ln}} = \frac{Mass_{MnSO_4 \text{ ln}}}{Mass_{water}} \rho_{water} \quad (A7)$$

You may wish to assume that the higher concentration solution has a proportionately higher density and just make one measurement of density. However, since you did not make the solutions yourselves, you may also wish to measure the density of both solutions as a check of the relative concentrations, and as a method with which to determine an error for the stated concentration.

3. Quincke's experimental method

On an atomic level, the force F acting on a magnetic dipole of moment m due to an applied magnetic field B is

$$\vec{F} = \nabla(\vec{m} \cdot \vec{B}) = \nabla(m_x B_x \hat{i} + m_y B_y \hat{j} + m_z B_z \hat{k}) \quad (A8)$$

Therefore the force *per unit volume* experienced at a point in the liquid in the U-tube is given by

$$F = \frac{\chi}{\mu_0} \nabla(\vec{B} \cdot \vec{B}) = \frac{\partial B_x^2}{\partial x} \hat{i} + \frac{\partial B_x^2}{\partial y} \hat{i} + \frac{\partial B_x^2}{\partial z} \hat{i} + \frac{\partial B_y^2}{\partial x} \hat{j} + \frac{\partial B_y^2}{\partial y} \hat{j} + \frac{\partial B_y^2}{\partial z} \hat{j} + \frac{\partial B_z^2}{\partial x} \hat{k} + \frac{\partial B_z^2}{\partial y} \hat{k} + \frac{\partial B_z^2}{\partial z} \hat{k} \quad (A9)$$

providing B is in the horizontal z -direction throughout the volume occupied by the liquid. This equation can also be written

$$F_{x-uvol} = \frac{\chi}{2\mu_0} \cdot \frac{d(B_x^2)}{dx} \quad (A10)$$

Equation (A10) can also be derived by considering the stored energy, since the force is the negative of the gradient of the energy, which is proportional to B^2 through the term $\frac{1}{2} \vec{B} \cdot \vec{H}$ per unit volume.

The force acting on an element of area A and length dx of the column of liquid is $F_x A dx$ so the total force F on the liquid is,

$$F = A \int F_{xvol} dx = \frac{A\chi}{2\mu_0} \int \frac{d(B_z^2)}{dx} dx = \frac{A\chi(B^2 - B_0^2)}{2\mu_0} \quad (\text{A11})$$

where the integral is taken over the whole liquid. This means that B is equal to the field at the surface between the poles of the magnet and B_0 is the field at the other surface, away from the magnet.

The liquid moves under the action of the total force F until it is balanced by the pressure exerted over the area A due to a height difference $2h$ between the liquid surfaces in the two arms of the U-tube. Allowing for the susceptibility χ_a and density ρ_a of the air that the liquid displaces, it follows that,

$$\frac{A(\chi - \chi_a) \cdot (B^2 - B_0^2)}{2\mu_0} = 2Ah(\rho - \rho_a)g, \quad (\text{A12})$$

where g is the acceleration due to gravity, so that

$$(\chi - \chi_a)(B^2 - B_0^2) = 4\mu_0 h(\rho - \rho_a)g \quad (\text{A13})$$

Thus equation A13 shows that by plotting h as a function of B^2 , the susceptibility χ can be determined directly from the slope of the graph.

In practice, *the corrections due to air are negligible*. However there will also be a small but significant diamagnetic (i.e. *negative*) contribution to the susceptibility mainly due to the water. The total susceptibility of the solution is then given by $\chi = \chi_{Mn} + \chi_{water}$ assuming that the number of water molecules per unit volume is not very different in the solution from that in pure water.

Scrupulous cleanliness of the U-tube is essential since unknown contamination will also contribute to the total susceptibility, in an unknown way. The tube should be cleaned distilled water and dried with compressed air. Several sets of measurements should be made to enable an assessment of the error. False readings can arise from liquid running down the tube or sticking to the sides. Carefully swab down the inside of the U-tube with a cotton bud, to ensure that there are no droplets of liquid which might interfere with the plastic spacers on the rod which measures the height of the meniscus. Do not use the U-tube for longer than one laboratory period without recleaning. After cleaning you may ask a laboratory technician to dry the tube for you with compressed air.

4. Measuring magnetic field with a Hall probe

The control of current flowing through the magnet is achieved using a *variac* whose voltage can be set. The current flowing at a particular voltage can be measured on the dial located at the back of the magnet.

You should calibrate the magnetic field against magnet current using the digital Hall probe. Position the probe so that it gives positive values of B and use the stand provided so that it remains in the same position throughout your calibration. If you record your calibration data with sufficiently small increments of current this will provide the best definition of the entire curve, which will be linear for small values of current and then the slope will decrease as magnetic saturation occurs in the material of the pole pieces.

The magnet will run continuously with a current of 5A; for short periods at 10A and for very brief periods at 15A. Note there may also be some magnetic hysteresis present and for a given current, the field may be slightly different, depending on whether the current is increasing or decreasing. The magnetic saturation means that the highest values of current do not produce an equivalent increase in the values of the magnetic field. However you should measure the highest fields (subject to the current restrictions given above) since these will give the largest changes in the height of the magnetic liquids.

Use the Hall probe to determine if there is any variation of B across the region of the magnet pole pieces and how the measured field depends on the angle that the probe makes with the pole pieces. You should use this information to help estimate the error in measuring B as a function of current.

Note also that the S.I. unit of B is the Tesla, however the Hall probes are calibrated to record in kOe, kilo-Oersted's. The conversion factor is $1 \text{ T} = 10 \text{ kOe}$. In the event of any problems consult a demonstrator.

4. Using PolyFit

To allow you to generate an analytical function, from your calibration data, that describes the field B as a function of current I , a polynomial fitting plug-in (for excel) is available on the second year website. The software is contained within the zip file "PolyFit". You should download the zip file from the list of documents on the right hand side of the second year lab homepage. You should save the plugin "XIXtrFun" to your user space and then install it via the Excel start menu – options – addins. The Excel template "PolyFit_example.xls" in the zip folder contains an excel program written using the plugin and some example calibration data for the magnet. If "XIXtrFun" is installed correctly this example file should show a 6th order polynomial fit as a red line overlayed on black data points. If you have think you have installed the plugin correctly, and this "fit" is not working please consult a demonstrator.

You should copy your calibration data to replace the example data in their respective columns. You can insert or delete rows as necessary. However, please ensure that all rows contained inside the black box include data, and that all data is entered inside the black box. Once you have fitted your calibration data the polyfit program will show the coefficients for the degree of polynomial that you have chosen. You should use these coefficients to recreate a calibration function that relates the current you measure on the electromagnet to the B field within it, for your *real* experimental measurements.

The 2007 version of Excel actually includes a polynomial fitting function, however the precision that the coefficients are reported to is not sufficient to reproduce the calibration curve, and is of no use in this experiment.

Pre-lab multiple choice questions

Q1 At which location is the greatest contribution to the resultant vertical force, acting on the Mn^{2+} solution

	A
	B
	C
	D

Q2 In which sub-shell (A-E) are electrons present in the following ions and atoms.

Mn^{5+} $p = g\sqrt{J(J+1)} = 1.63$

	s	p	d
1	$\uparrow\downarrow$		
2	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	
3	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	A B C D E
4			

$J=L+S$ $S=1$ $L=3$

Mn^0 $p = g\sqrt{J(J+1)} = 5.92$

	s	p	d
1	$\uparrow\downarrow$		
2	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	
3	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	A B C D E
4	$\uparrow\downarrow$		

$J=L+S$ $S=5/2$ $L=0$

V^{2+} $p = g\sqrt{J(J+1)} = 0.77$

	s	p	d
1	$\uparrow\downarrow$		
2	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	
3	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	A B C D E
4			

$J=L+S$ $S=3/2$ $L=3$

Cu^0 $p = g\sqrt{J(J+1)} = 3.55$

	s	p	d
1	$\uparrow\downarrow$		
2	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	
3	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	A B C D E
4	$\uparrow\downarrow$		

$J=L+S$ $S=1/2$ $L=2$