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Frequency dependency of magnetic susceptibility in SP magnetite grains

Hamedpour Darabi, M.[1*], Noorafshan, M.[2] and Dearing, J.[3]

[1] Assistant Professor, Department of Physics, Hormozgan University, Iran
[2] Lecturer, Department of Physics, Hormozgan University, Iran
[3] Professor, Department of Geography, University of Liverpool, England

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Abstract

Using a Magnetic Property Measurement System (MPMS), we measure magnetic susceptibility continuously at frequencies from 0 to 1000 Hz for three different superparamagnetic (SP) grain sizes of magnetite (5nm, 7 nm and 10 nm) suspended in hydrocarbons (Ferrofluids). Our results confirm non-zero values of frequency-dependent susceptibility in the fine tail of nano-sized grains and provide new empirical data for the degree of interaction between SP grains (nano particles) affecting magnetic susceptibility and frequency-dependent susceptibility.

Key words: Ferro fluid, Nano particles, Frequency dependency

وابستگی بسامدی خودپذیری مغناطیسی نانو ذرات مگنتایت

محمد حامدپور دارابی[۱]، مریم نورافشان[۲] و جان دیرینگ[۳]

[۱] استادیار، گروه فیزیک، دانشگاه هرمزگان، ایران
[۲] مربی، گروه فیزیک، دانشگاه هرمزگان، ایران
[۳] استاد، گروه جغرافیا، دانشگاه لیورپول، انگلستان

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چکیده

با استفاده از دستگاه اندازه‌گیری خواص مغناطیسی (MPMS)، خودپذیری مغناطیسی سه اندازه ۵، ۷ و ۱۰ نانومتر از ذرات مگنتایت معلق در هیدروکربن (که فروسیال نامیده می‌شوند، Ferrofluids) را به‌طور پیوسته از بسامد ۰ تا ۱۰۰۰ هرتز اندازه گیری کرده‌ایم. نتایج به‌دست آمده، وابستگی خودپذیری مغناطیسی این ذرات ریز در حد نانو را به بسامد میدان مغناطیسی تأیید کرده است و نتایج جدیدی در خصوص میزان اندرکنش ذرات SP به‌دست می‌دهد.

واژه‌های کلیدی: بستگی، بسامد، نانو، فروسیال

1 INTRODUCTION

In an AC magnetic measurement, a small AC drive magnetic field is superimposed on the DC field causing a time-dependent magnetic moment in the sample and therefore yields information about magnetisation dynamics and characterizing magnetic particles which is not obtained in DC measurements. The field of the time dependent moment induces a current in the pickup coil, allowing measurements without sample motion. The detection circuitry is configured to detect only in narrow frequency band, normally at the fundamental frequency (that of the AC drive field). At small AC fields the induced AC moment is M_{AC} = (dM/dH) . (H_{AC} sin(ωt)) in which H_{AC} is the amplitude of the driving field, ω is the driving frequency and dM/dH, the slope of the M(H) curve, the quantity of interest in AC measurements, called magnetic susceptibility (κ). Low field

*Corresponding author: Tel:0761- 7660055 Fax: 0761- 7660055 E-mail: Darabi@ut.ac.ir

magnetic AC susceptibility (κ) measurements can also help to identify the concentration and grain size distribution of ferromagnetic minerals in a sample (Thompson and Oldfield, 1986). Frequency dependency of magnetic grains measured, ($\kappa_{fd}\% = (\kappa_{lf} - \kappa_{hf} / \kappa_{lf})*100$), at two frequencies (low frequency, κ_{lf}, and high frequency, κ_{hf}, magnetic field) shows considerable variation with grain size, especially across the superparamagnetic (SP) and stable single domain (SSD) boundary (Dearing *et al.,* 1996). The effect of interaction on magnetic properties is explicitly discussed by some people (Dormann et al., 1999; Virdee, 1999; Muxworthy, 2001). Muxworthy (2001) examined weak interaction for an assemblage of grains near SP-SSD threshold (known as V_b, blocking volume) and showed that weak interaction increase anisotropy between SP grains, it consequently decreases V_b and the effect of this decrease is to reduce both κ and κ_{fd}%. The useful distinction is made between dynamic interactions among unblocked SP grains where V_b is reduced, and static interactions between blocked SP grains where V_b is increased. This is also described in details by Muxworthy (2001).

Nano-scale phenomena make testing theory through empirical analyses challenging. In this work we use a limited number of controlled grain size samples of dried ferrofluids (DFF) to determine: first, κ_{fd}% values as a function of grain size in the range of 5-10 nm; second, the effect of grain interaction on κ_{fd}%; and third, the effect of grain size distribution on κ_{fd}% values in a mixed sample.

2 METHODS AND MATERIALS

Ferrofluids (FF) are concentrated fluids consist of nanometre sized magnetic particles held in suspension in a carrier liquid. They have been coated by a surface active layer to reduce the effect of static interaction. The carrier liquid is selected to meet particular application that in this work is non-magnetic hydrocarbon liquid. FF packages were obtained from the Liquid Research Limited Company (www.liquidsresearch.com) consisting of spherical magnetite (Fe_3O_4) grains. Three samples were used in the study (Table1), with different mean grain diameters (5 nm, 7 nm and 10 nm). The variance in size for each sample is small (1sd ~ 0.45 nm) which means that none of the samples should contain grain sizes normally associated with maximum κ_{fd}% at the viscous SP/SSD boundary.

Sample preparation for magnetic susceptibility measurements of ferrofluids using the MPMS requires careful consideration. If the measurements are to provide valid inference about the magnetic behaviour of nano-sized grains in natural soils and sediments, normally in dried form, FF samples should also be dried (Maher, 1988). To address this we made measurements on both original wet FF and DF, assuming that drying will reduce inter-grain distances and increase self-demagnetizing effects. Figure 1 shows test measurements for 7 nm samples in FF and DF states. Although it shows a 60% reduction in the slope of the κ-logf curve for DF compared to FF (this will be discussed further in the following section), but both curves show similar behaviour with matching peaks, therefore the rest of measurements are performed on DF samples. DF samples were produced using a procedure in an argon vacuum so as to avoid the risk of magnetite oxidation.

Table1. Ferrofluid specifications provided by the manufacturing company.

Product code	Magnetite Content by weight	Boiling Point	Specific gravity	Viscosity at 27°C	Saturation Magnetisation of magnetic concentration (G)
FHJS1 (10nm)	< 20%	< 200 °C	0.9 – 1.0	< 5 cp	200
FHYs1 (7nm)	< 10%	180 – 200 °C	0.9 – 1.0	< 5 cp	200
FHYS1 (5nm)	< 10%	180 – 200 °C	0.9 – 1.0	< 5 cp	200

Measurements were made on an MPMS system with a 7 Tesla super-conducting magnet (Quantum Design http://www.qdusa.com), capable of making magnetic measurements with an automatic temperature sweep from temperatures at liquid He to room temperature. Measurements in this work have been performed in a constant temperature of 300K. AC susceptibility measurements can be measured at frequencies between 0.1 Hz and 1 kHz with a sensitivity of 2×10^{-8} emu at Zero Tesla. DC magnetization measurements can be performed on this equipment with an absolute sensitivity of 1×10^{-8} emu at 2500 Oe.

κ is measured in a magnetic field with variable frequency (0.1-1000 Hz) for samples of individual mean grain sizes (5 nm, 7 nm and 10 nm). An important element in the theory of frequency-dependent susceptibility is the effect of grain size distribution. Thus, we also create a mixture of the three grain sizes in equal volumes (0.333: 0.333: 0.333) before drying.However, the content of magnetite in the 5 and 7 nm samples by weight is 0.1, and 0.2 for the 10 nm sample. Therefore, the mass of the dried mixed sample consists of two parts of the 10 nm sample and one part of each of the 5 and 7 nm samples. To show the effect of interaction we calculate the susceptibility of a virtual sample by adding the susceptibility values of the three individual FF samples using the same mass ratio as the mixed sample. The virtual sample has the same mass as the mixed sample and therefore its calculated susceptibility can be compared with the mixed susceptibility value.

Three other samples were measured for comparison with the FF: a sample of dysprosium oxide (Dy_2O_3, used as the MPMS calibration sample); a natural hematite crystal; and a natural highly magnetic surface soil from SW England (LZ2-18).

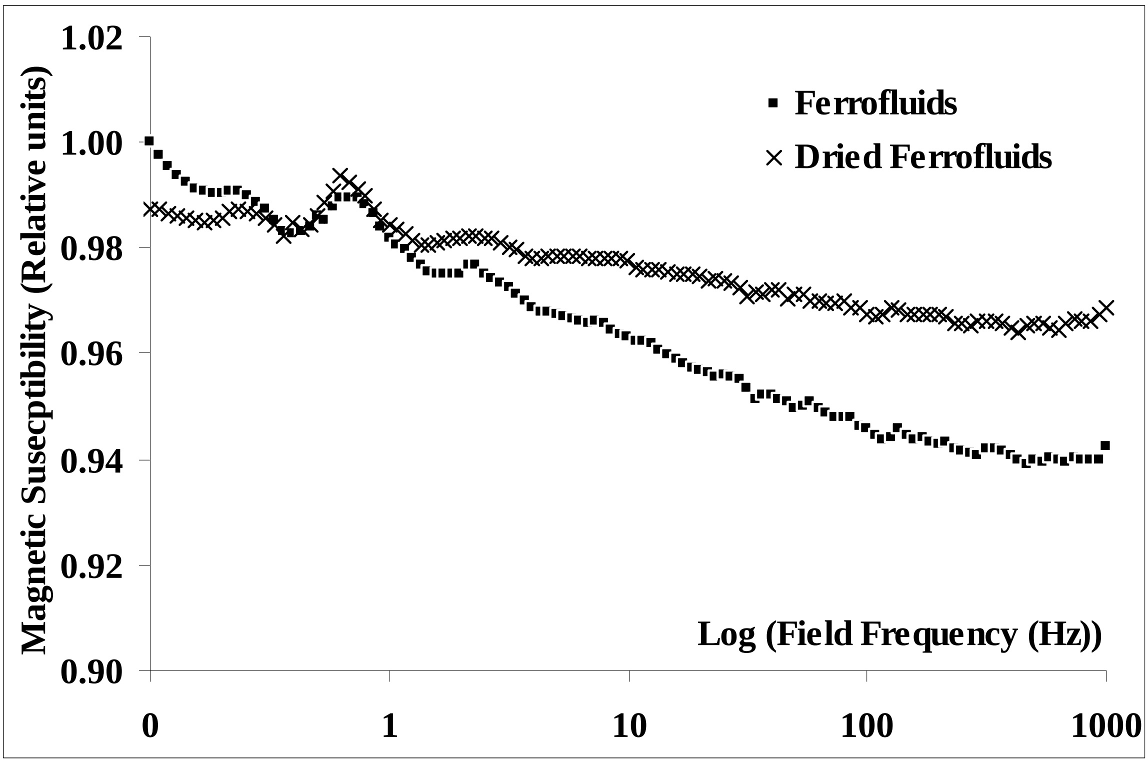


Figure 1. Room temperature magnetic susceptibility (κ) measurements in a frequency range (logf) of 0.1 to 1000 Hz for 7nm Ferrofluid and dried Ferrofluid samples.

3 RESULTS AND DISCUSSION

3-1 GRAIN INTERACTION EFFECTS

The shallower slope for 7 nm DF suggests that enhanced grain interaction through drying causes a relative reduction in κ_{fd}% by 50% compared to FF (Figure 2). In the FF, grains are free to move and we may assume that there is no measurable grain interaction. Thus the effect of drying is to reduce κ_{fd}% values through an increase in self-demagnetizing effects, as argued for natural soils (Dearing et al., 1996).

Figure 2 compares the absolute values of magnetisation for the mixed sample, virtual sample and the difference between them. The difference is about 10^{-3} emu for all frequencies which is equivalent to 25-27% of the mixed sample susceptibility value. This difference is 10^{3} times bigger than the measurement error calculated by MPMS (for mixed data the standard deviation (sd) varies between $1_{\times}10^{-7}$ to $3_{\times}10^{-6}$ emus). A non-interactive regime is expected if the difference between the κ of the mixed sample and the virtual sample is within an acceptable error (say 1 sd) of the actual measurements. Therefore our results exhibit an interactive regime.

Slope reduction of the curves in the 7nm test (a consequence of drying and therefore amplifying grain interactions) is consistent with the reduction in κ (seen in Figure 2 to suggest the existence of grain interactions). Therefore, we deduce that the effect of interaction results in the reduction of both κ and κ_{fd}%. This means a probable reduction in V_b and consequently a dynamic interaction regime rather than a static one (Muxworthy 2001).

3-2 FREQUENCY- DEPENDENT SUSCEPTIBILITY

Figure 3 shows the κ-logf measurements for dried samples of 5 nm, 7 nm, 10 nm grain sizes, the sample mixture, the Dy_2O_3 sample and the hematite crystal. All samples, except, the 5 nm one show declining κ values with increasing frequency (logf). All the samples show a tendency for a peak in values at relatively low frequencies (~2-5 Hz) and there is an upward trend in values for the magnetite samples at relatively high (~>500 Hz) frequencies. The similar behaviour for hematite and Dy_2O_3 suggests that these features are probably nonlinear responses of the equipment.

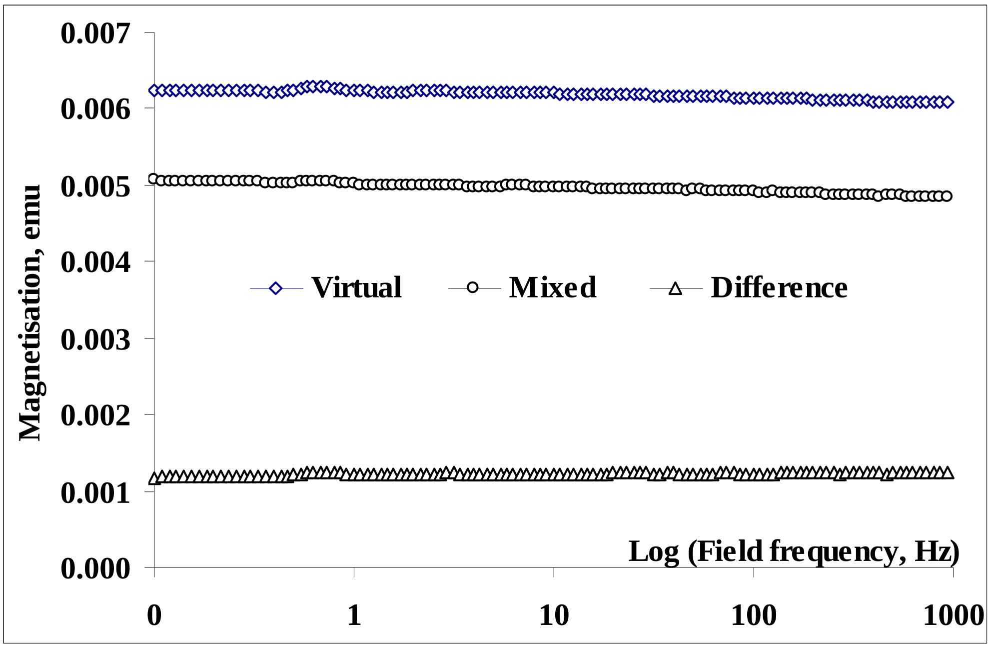


Figure 2. Magnetization-logf curves for mixed and virtual samples and the difference between them.

The gradient of the curves indicates the degree of frequency dependency. In the frequency range 47-470 Hz, the 5 nm sample shows essentially no frequency dependency effect. But negative slope gradients are observed for the other magnetite samples with the steepest gradient observed in the mixed sample. It is clear that the 5 nm particles are not blocked even up to 1000 Hz, while the negative slopes for the other samples indicate the blocking effect of the larger grains measured in the frequency range 1-850 Hz. Table 2 summarizes the average frequency dependencies (κ_{fd}%) measured between two frequencies a decade apart of 47- 470 Hz (This decade is chosen to meet the history of the Bartington dual frequencies of 470-4700 Hz and be in the stable varying rang of susceptibilities in Figure 5). Although the dependency is low for the three single grain sizes the values increase roughly linearly with grain size (Figure 4). The κ_{fd}% values for the mixed sample are higher than the values for any of the single dried samples (Table 2). This suggests that either grain interaction effects are smaller in larger particles or that a mixture of different grain diameters exhibits less grain interaction than a narrower distribution of grain sizes. Natural soil samples contain a wide range of secondary ferrimagnetic minerals across the SP and SSD grain sizes. The MPMS scan of susceptibility (Figure 5) for highly magnetic topsoil from SW England (LZ2-18) shows a large κ_{fd}% value compared to the other samples (8.6 %). A higher κ_{fd}% value for mixed sample (1.4 %) predicts an effective grain size about 10.5 nm (Figure 4). This size can be considered as a measure of grain size distribution width, the wider the grain size distribution the greater the effective grain size.

Table 2. Frequency dependency for different grain sizes measured by MPMS.

Grain size / Sample	Magnetisation at 47Hz (emu)	Magnetisation at 470 Hz (emu)	Frequency dependency (κ_{47}-κ_{470}/ κ_{47})*100
5 nm	7.94E-04	7.95E-04	-0.08004
7 nm	8.98E-04	8.93E-04	0.526281
10 nm	6.97E-03	6.88E-03	1.269431
Mixed	4.93E-03	4.86E-03	1.41594
LZ2-18	8.74E-05	7.99E-05	8.573325
Hematite	3.85E-05	3.84E-05	0.288039
Dy2 O3	2.02E-05	2.02E-05	0.103303

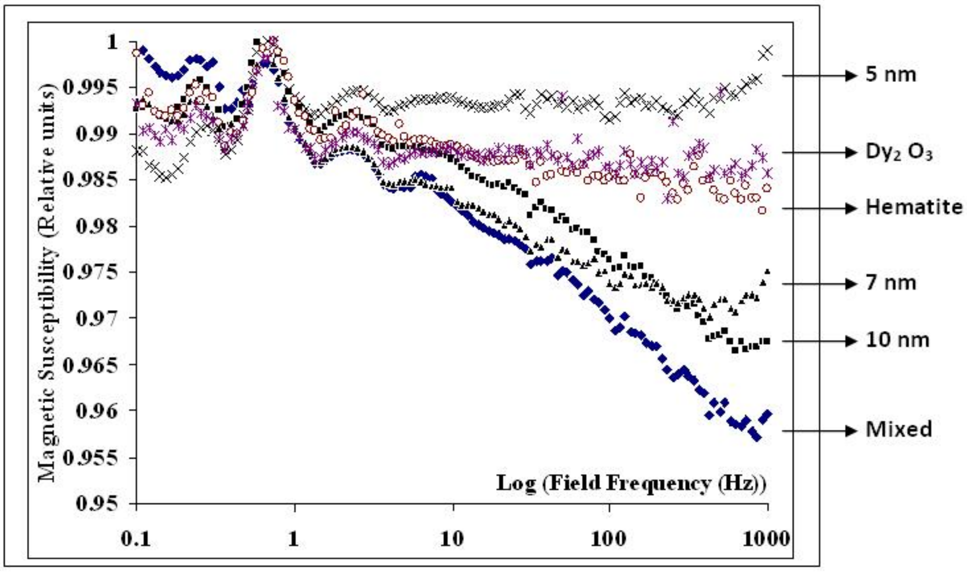


Figure 3. Magnetic susceptibility (κ) versus wave frequency (logf) for three dried Ferrofluids (5nm, 7nm and 10nm), the mixed samples, Dy_2O_3, and a hematite crystal.

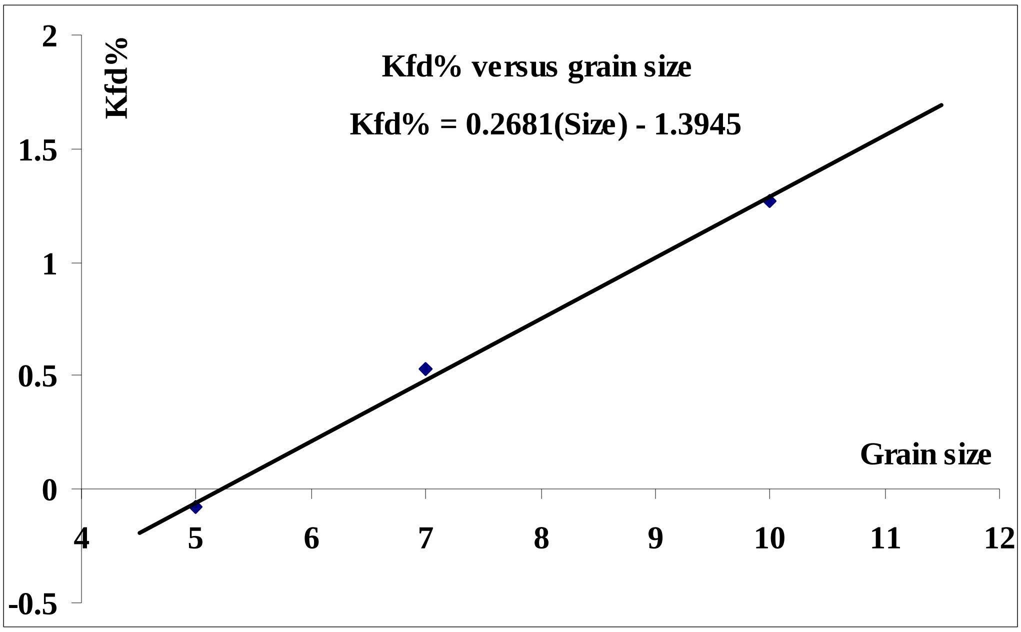
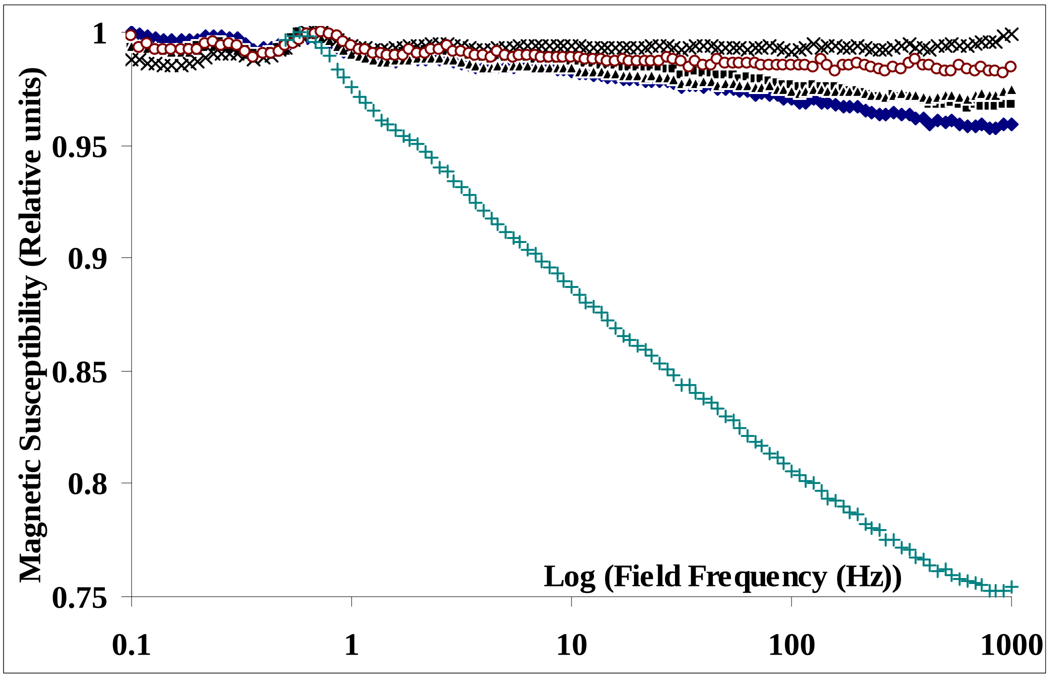


Figure 4. Relationship between κ_{fd}% and grain size samples based on 47-470 Hz frequency range.



LZ2-18

Figure 5. Comparison of κ-logf curve of LZ2-18 with synthetic samples.

3-3 SUSCEPTIBILITY MODELS

Environmental systems often contain SP grains that show a frequency dependency of magnetic susceptibility in low AC fields. These systems contain grains smaller than SP as well as greater than SSD sizes and they seem to show no frequency dependency when AC field is applied (Bathal and Stacey, 1969). Therefore κ_{fd}% of SP grains could be an important tool for determining grain size distribution and concentration in the sample (Dearing, 1994). There are many theoretical models for κ_{fd}% of SP grains, some describe non-interacting systems and some consider the influence of magnetic grain interaction on magnetic properties (e.g. Virdee, 1999). Dormann-Bessais-Fiorani model (DBF model, Dormann et al., 1988) is a modified version of Worm non- interacting model (Worm, 1998) which considers interaction effect by adding interaction energy to the anisotropy energy for non-interacting state. Dormann et al. (1999b) applied this model on experimental results to consider grain interaction. In the present study also we apply DBF model as our results noticeably show the presence of interaction.

In a non-interacting system, the magnetic susceptibility of SP grains (κ_{sp}) in an AC field derived by N'eel (1949) and Worm (1998) as follows:

$$\kappa_{sp} = [M_s \tanh(M_s V M_s h/3kT)]/h(1+\omega^2\tau^2)$$

For small h we have:

$$\kappa_{sp} = M_s^2 V \mu_0 / 3kT(1+\omega^2\tau^2)$$

In which ω is wave number, μ_0 is magnetic permeability, M_s is spontaneous magnetisation, k is Boltzman constant and T is temperature. τ is relaxation time which is driven by Neel (1949):

$$\tau = \tau_0 e^{-(E_B / kT)}$$

In which τ_0 is atomic arrangement time. It is chosen 10^{-9}s for magnetite (worm 1998). E_B is the barrier energy for magnetic dipole moment to switch its direction (Worm 1998). It is equal to the energy of anisotropy when grains are non-interacting.

$$E_B = E_a = \mu_0 M_s V H_k$$

In the case of interacting grains, each SP grain is influenced by magnetic dipole of neighbouring grains as well as the ambient magnetic field (Dunlop and West, 1969). Therefore, an interacting field also has to be considered in addition to the grain response to the external field. The behaviour of a bulk of SP grains with randomly distributed magnetic dipoles is considered in two steps by Dormann *et.al.* (1999 a, b). The first step is to consider a non-interacting SP grains model, Worm model, for calculating pure super paramagnetic susceptibility (Worm, 1998) and the second step is to add the effect of weak interaction between SP grains to the worm model (Dormann, *et.al.,* 1999a).

Dormann estimates the average interaction potential energy over all possible arrangements of particles and shows that the dynamic interaction is equivalent to an increase in particle anisotropy of non-interacting N'eel model (1949). As the first approximation, for only nearest neighbour's, barrier energy can be written as follows (O'Grady et.al., 1993):

$$E_B = E_a + E_{in}$$

In which E_a is the anisotropy energy for non-interacting state, E_{in} interaction energy:

$$E_{in} = n\, \mu_0\, M^2_s V_M\, a_1\, L(\mu_0\, M^2_s V_M\, a_1 / KT)$$

In which V_M is the mean volume of the SP particles,

$$a_1 = V_M <3\cos^2 \psi - 1> / <d_{cc}^3>$$

n is the average number of nearest-neighbours, ψ and d_{cc} shows the position of the nearest neighbour. The value of ψ is not significant compared to the other variables and the term $<3\cos^2 \psi - 1>$ varies between 1 and 2, for simplicity ψ was held constant at room temperature. L is Langevin function. $<d_{cc}>$ is the mean centre-to-centre interparticle separation. It is normally written as $d_{cc} = d\, d_0$, where d_0 is average diameter of the SP grains and d is relative distance in terms of d_0. τ_0 is weekly affected by the interaction field. This effect is relatively small and in the following calculations it is assumed to be constant (Dormann et al., 1999b).

Figure 6 produced according to DBF interacting model using a certain and similar value of n and d for the three grain sizes of 5, 7, 10 nm and the mixed samples over the frequency range of 0-1000 Hz. Our experimental and theoretical results show a similar trend of κ and κ_{fd}% variation with the applied field frequency. This suggests that DFB is probably a proper theoretical model for our experimental data. It is consistent with Muxworthy (2001) calculation for weakly interacting grain distributions.

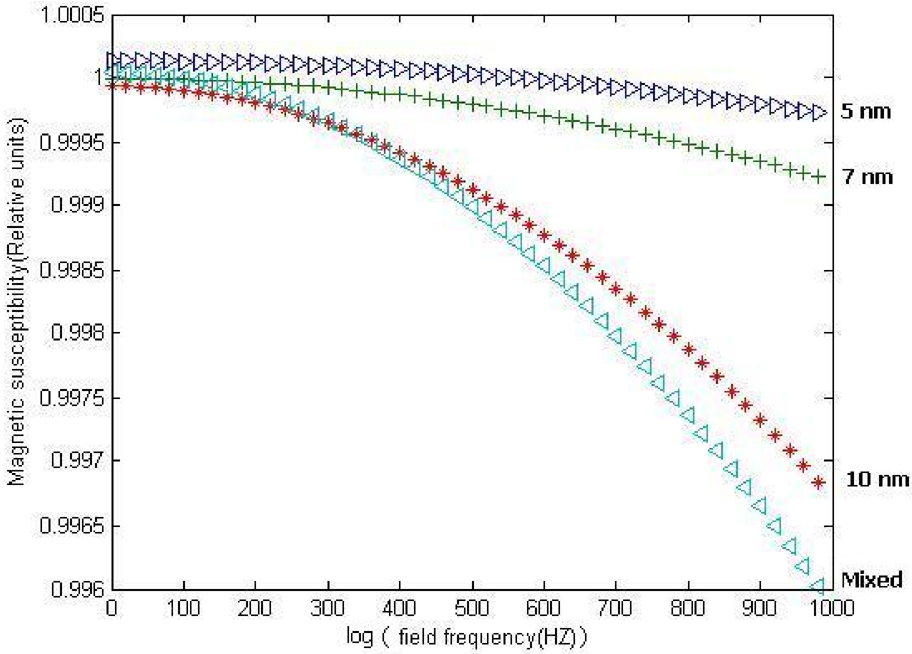


Figure 6. Magnetic susceptibility (κ) produced by DBF Model versus wave frequency (logf) for three sizes (5nm, 7nm and 10nm) and the mixed samples.

3-4 FREQUENCY DEPENDENCY

The limited data presented here are consistent with theory (Dormann et al., 1988; Muxworthy, 2001) and deductions from empirical studies (eg. Oldfield *et al.,* 1985) that predict low but non-zero κ_{fd}% values in the 5 nm range of ferrimagnetic minerals, increasing with grain size up to 10 nm. Measurable κ_{fd}% values for grains 5-10 nm confirms previous theoretical considerations (Dearing et al., 1996; Wörm, 1998; Muxworthy, 2001) that frequency-dependent measurements are not related simply to the presence of viscous grains lying within a very narrow range at the SP/SSD boundary.

Enforced grain interaction by drying previously weekly-interacting grains causes reduction of κ_{fd}% values by ~25%. This is in line with Muxworthy (2001) findings for weakly interacting grain distributions. But the observation that the κ_{fd}% value is higher than any of the component grains in a mixture is counter to expectations that a wide grain distribution will generally show higher κ_{fd}% values. Higher κ_{fd}% values in wide grain assemblages may thus indicate lower interaction effects either through increased interaction distances or reduced numbers of nearest grain neighbours. More analyses are needed to confirm this single observation, but it does raise the possibility that theoretical curves of interaction effects for SP grain size distributions may not directly map on to actual grain size distributions and interaction effects in soils. Linked to this, the limited data presented here do not support specific calculations (Muxworthy, 2001) that predict enhanced κ_{fd}% values due to interactions in grain size ranges <6 nm.

4 CONCLUSIONS

For measurements made on the MPMS, calculated κ_{fd}% values of nano-sized magnetite grains appear to increase roughly linearly with mean grain diameter over the range 5-10 nm. Although all the magnetite grain sizes measured lie in the SP size range, it seems that for these magnetite grains we can assign a lower boundary for non-frequency dependent grains at <5 nm.

At all frequencies between 1 and 1000 Hz the susceptibility value for a mixed sample of known grain sizes is less than the calculated value from the virtual sample. This means that the effect of interaction reduces κ to about 25% of the susceptibility of a non-interactive magnetic grain system.

Enhanced values of κ_{fd}% in a mixture of the grain sizes suggests that widening the distribution of grains may result in reduced grain interaction as a result of changing interaction distances and the numbers of grain sizes interacting with each other.

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