On the determination of magnetic grain-size distributions of superparamagnetic particle ensembles using the frequency dependence of susceptibility at different temperatures

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Accepted 2005 February 8. Received 2004 December 8; in original form 2004 May 14

SUMMARY

Magnetic grain-size and coercivity distributions of a superparamagnetic (SP) particle ensemble together determine its frequency dependence of susceptibility (FDS). Investigating the mathematical theory of this dependence leads to a general dispersion relation between real and imaginary parts of the complex susceptibility for SP particle ensembles, which extends the previous treatment by Néel. Using the new theory, it is demonstrated that the inverse problem of determining the combined grain-size and coercivity distribution from FDS measurements is not uniquely solvable. The inversion of the FDS at one temperature can be described by a deconvolution integral, the kernel of which is analytically calculated. The deconvolved FDS corresponds to an energy barrier distribution. Only using *a priori* assumptions about the relation between particle volume and coercivity it can be interpreted in terms of a volume or grain-size distribution. In order to deconvolve natural rock measurements, a semi-analytical parametric deconvolution method has been developed, which allows to reconstruct the SP grain-size distribution even from relatively noisy data. Dense measurements of FDS at several temperatures can be used to check for the applicability of the above theory. Observed deviations can be interpreted in terms of magnetostatic particle interaction. A quantitative estimate is presented, which allows to determine the average interaction field together with the volume distribution.

Key words: deconvolution, environmental magnetism, frequency-dependent susceptibility, measurement techniques, stochastic resonance, superparamagnetism.

1 INTRODUCTION

During the last two decades the results from environmental magnetism have been recognized to be of major importance for the study of Quaternary climate change (Thompson & Oldfield 1986; Maher & Thompson 1999; Evans & Heller 2003). The ubiquitous magnetic mineral fraction represents a reliable fingerprint of source and transport processes in marine as well as in continental sedimentary systems and, in addition, allows to reconstruct post-depositional processes (Tarduno 1994). Therefore, detailed knowledge of grainsize-dependent magnetic characteristics is an essential prerequisite for environmental studies. In particular, the submicroscopically fine ferrimagnetic fraction provides information about iron mobilization, migration and precipitation during soil formation (Le Borgne 1955; Mullins & Tite 1973; Dearing et al. 1996) and also acts as sensitive magnetic recorder of palaeoclimatic and palaeoenvironmental change in marine sedimentary environments (Frederichs et al. 1999). Fine magnetite grains also constitute the physical basis for magnetoreception in living organisms (Blakemore 1975; Kirschvink et al. 1985; Wiltschko & Wiltschko 1995). Magnetite particles having grain sizes below approximately 30 nm cannot support a stable

magnetic moment at room temperature due to thermally induced spontaneous magnetization changes (Néel 1949). This behaviour is known as superparamagnetism (SP) because the particles behave similar to paramagnetic atoms although their magnetic moment is by many orders of magnitude larger (Bean & Livingston 1959). Stephenson proposed a theoretical method for the determination of SP grain-size distribution f(v) using a polynomial representation of f(v) (Stephenson 1971). In the same paper he proposed also a practical method of its determination based on measurement of the decay of thermomagnetization (TRM) or saturation remanence $M_{\rm rs}$ as the sample warms up in zero magnetic field H. Worm and Jackson used the latter method to determine the grain-size distribution of the SP fraction of three extraordinary tuff samples (Worm & Jackson 1999). Stephenson's method determines the coefficients of some specific form for the distribution function f(v) by comparing theoretical predictions with experimental results (Stephenson 1971). It relies upon a priori knowledge about the possible distribution functions, a fixed relation between coercivity and particle volume, and the complete lack of interaction effects. It has not yet been investigated whether more exact and rigorous information can be obtained by inverse modelling of the distribution function f(v) by using large

experimental data sets. It is well known that very detailed information can be obtained from the measurement of the frequencydependent susceptibility (FDS) at a number of temperatures (Stephenson 1971; Eyre 1997; Worm & Jackson 1999). Measuring room temperature FDS at only two frequencies (usually 400 Hz and 4 kHz) is a standard procedure in environmental magnetism to infer the presence of SP particles (Thompson & Oldfield 1986). Its problems and limits have been thoroughly discussed (Dabas et al. 1992; Dearing et al. 1996; Eyre 1997; Worm 1998). The present article gives a complete analysis of the problem of determining the grain-size distribution of SP particle ensembles from FDS measurements at several temperatures for the case of non-interacting ideal Stoner-Wohlfarth (Stoner & Wohlfarth 1948) single-domain (SD) particles. Moreover, it is shown that not even an arbitrarily dense data set allows to infer the 2-D grain distribution in volume and coercivity. On the other hand, we demonstrate that magnetostatic particle interaction distorts the FDS signal and derive a new method to estimate average interaction field and magnetic freezing temperature of the SP particle ensemble. It should be considered that FDS measurements at several temperatures could be much easier included into a routine measurement scheme than other low temperature measurements which are usually applied to obtain SP grain-size distributions.

2 BASIC FACTS FROM THE THEORY OF FDS

In SD particles below some critical size the exchange interaction enforces coherent rotation of all quantum mechanical spin moments. This case of coherent rotation is valid throughout for SP magnetite particles (Néel 1949; Mullins & Tite 1973; Dabas *et al.* 1992; Winklhofer *et al.* 1997). In Néel's (Néel 1949) theory of superparamagnetism it is assumed that an uniaxial SD particle is in one of two possible states which in zero external magnetic field are separated by an energy barrier E_b , small enough to be overcome by thermal activation energy k_BT , where k_B denotes the Boltzmann constant and Tis the absolute temperature. The name superparamagnetism refers to the fact that the physical description of such a non-interacting magnetic particle ensemble is analogous to the theory of paramagnetism.

For an ensemble of particles, each of which has the same volume v and energy barrier E_b , the Ising approximation gives the average magnetization

$$M(H, T, v) = n v M_s \tanh\left[\frac{\mu_0 M_s v H}{k_B T}\right],$$
(1)

where *H* is the magnetic field, M_s is the saturation magnetization and *n* denotes the number of particles per unit volume. Accordingly, c = nv corresponds to the volume concentration of the magnetic fraction. If the anisotropy axes of a particle ensemble are randomly oriented in space, the static initial susceptibility χ_0 is given by

$$\chi_0 = \frac{dM}{dH}(0) = \alpha(T) v^2 n = \alpha(T) v c, \qquad (2)$$

where $\alpha(T) = \frac{\mu_0 M_e^2(T)}{3k_B T}$. Though derived here using the simple Ising approximation, eq. (2) remains valid for uniaxial particles even if the magnetization varies continuously (Néel 1949).

In zero field the time-dependent average magnetization M(t) of a random ensemble of SP particles with the same E_b relaxes toward its equilibrium magnetization $M_0 = 0$ according to

$$\frac{dM}{dt} = -\frac{1}{\tau}M,\tag{3}$$

where

$$\tau = \tau_0 \, \exp(\epsilon/2),\tag{4}$$

and $\epsilon = E_b(T)/(k_BT)$ is the normalized (to the thermal energy) energy of the potential barrier and τ_0 is the spin relaxation time (Néel 1949). This equation assumes that the typical timescale of dynamic spin movement is small compared to τ and relaxation essentially is a thermally driven process. The energy barrier usually is expressed in terms of a microcoercivity $H_k(T)$ as

$$E_b(T) = \mu_0 H_k(T) M_s(T) v.$$
 (5)

According to (Brown 1959), the spin relaxation time τ_0 varies with volume and temperature:

$$\tau_0 = \frac{1}{\gamma' \mu_0 H_k} \sqrt{\frac{2\pi k_B T}{\mu_0 H_k(T) M_s(T) v}} = \frac{1}{\gamma' \mu_0 H_k} \sqrt{\frac{2\pi}{\epsilon}}.$$
 (6)

In this equation, γ' is defined as

$$\gamma' = \frac{\eta M_s}{(\eta M_s)^2 + \gamma^{-2}},\tag{7}$$

where γ is the gyromagnetic ratio and η is a damping constant the value of which is badly known. In order to resolve this uncertainty, Brown recommends to set $\eta = (\gamma M_s)^{-1}$ in practical applications (Brown 1963). As seen from (7), for this value $\gamma'(\eta)$ assumes its maximum equal to $\gamma/2$, while

$$\tau_0 = \frac{2\sqrt{2\pi}}{\gamma\,\mu_0\,H_k}\,\sqrt{\frac{1}{\epsilon}}\tag{8}$$

is minimal. Since for magnetite SD grains H_k typically is in the range of 10^4-10^5 A m⁻¹, the most likely value of τ_0 is $(10^{-9}$ to $10^{-8}) \epsilon^{-1/2}$. The values of ϵ considered here satisfy the condition $\omega \tau_0 \sim \exp(-\epsilon/2)$ or $\epsilon \approx -2 \ln \omega \tau_0$. The frequency range of usual FDS measurements is $0.1-10^5$ Hz, thus the corresponding range of ϵ is 10-50. Therefore, in good approximation we can set $\sqrt{\epsilon} \simeq 5$ and within the range of its inevitable uncertainty τ_0 can be considered as independent of ϵ .

In a static small magnetic field *H* the equilibrium magnetization is $M_0 = \chi_0 H$ and the relaxation is described by

$$\frac{dM}{dt} = -\frac{1}{\tau}(M - M_0) \Rightarrow \tau \frac{dM}{dt} + M = \chi_0 H.$$
(9)

When a time-dependent field $H(t) = He^{i\omega t}$ is applied, where ω is small with respect to $2\pi/\tau_0$, the 'equilibrium' towards which the sample relaxes varies with time as $M_0(t) = \chi_0 H(t)$. Substituting the latter into (9) yields Néel's (Néel 1949) expressions for the timevarying sample magnetization $M(t) = \chi(\omega) H(t)$ and susceptibility

$$\tau \frac{dM}{dt} + M = \chi_0 H(t),$$

($i\omega \tau + 1$) $\chi(\omega) = \chi_0.$ (10)

The second line results from substituting for H(t) and M(t). Thus, the complex FDS for an isotropic SP ensemble of particles, all of which have the same volume v and energy barrier ϵ , at a fixed temperature T is

$$\chi(\omega, \epsilon, v) = \chi_p(\omega, \epsilon, v) - i\chi_q(\omega, \epsilon, v)$$
$$= \alpha \left(\frac{v c}{1 + \omega^2 \tau^2} - i \frac{v c \omega \tau}{1 + \omega^2 \tau^2} \right), \tag{11}$$

where in the last term χ_0 is substituted using (2).

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3 FDS OF INHOMOGENEOUS PARTICLE ENSEMBLES

To obtain the complex FDS for a realistic SP ensemble containing particles with different volumes v and energy barriers ϵ , (11) must be integrated over all these volumes and energy barriers. To this end, the concentration c in (11) must be replaced by $c(\epsilon, v) dv d\epsilon$ which denotes the concentration of SP particles having their volume in the range [v, v + dv] and their energy barrier in the range $[\epsilon, \epsilon + d\epsilon]$. Of course, integrating $c(\epsilon, v)$ over ϵ and v gives the total volume concentration c. The ensemble's complex susceptibility now is

$$\chi(\omega) = \int_0^\infty \int_0^\infty \chi(\omega, \epsilon, v) \, dv \, d\epsilon = \alpha \int_0^\infty \int_0^\infty \frac{v \, c(\epsilon, v)}{1 + i \, \omega \tau} \, dv \, d\epsilon.$$
(12)

Because the volume integration affects only the nominator, this can be expressed in terms of

$$\overline{v}(\epsilon) = \int_0^\infty v \, c(\epsilon, v) \, dv, \tag{13}$$

where $\overline{v}(\epsilon) d\epsilon$ corresponds to an effective volume of particles with energy barrier within $[\epsilon, \epsilon + d\epsilon]$. With this convention, (12) becomes

$$\chi(\omega) = \alpha \int_0^\infty \left(\frac{\overline{v}(\epsilon)}{1 + \omega^2 \tau^2} - i \, \frac{\omega \tau \, \overline{v}(\epsilon)}{1 + \omega^2 \tau^2} \right) d\epsilon. \tag{14}$$

Using relation (4) and introducing the new variable $\lambda = -2\log(\omega\tau_0)$ yields a representation of $\chi(\lambda)$ in terms of convolutions

$$\chi(\lambda, T) = \alpha \int_0^\infty \frac{\overline{v}(\epsilon)}{1 + \exp(-(\lambda - \epsilon))} d\epsilon - i\alpha \int_0^\infty \frac{\overline{v}(\epsilon)}{2 \cosh \frac{\lambda - \epsilon}{2}} d\epsilon.$$
(15)

of the function $\overline{v}(\epsilon)$ with the kernels $K_p(x) = \frac{1}{1 + \exp(-x)}$ and $K_q(x) = \frac{1}{2\cosh\frac{3}{2}}$, correspondingly. By setting $c(\epsilon, v) = 0$ and consequently $\overline{v}(\epsilon) = 0$ for $\epsilon < 0$, the lower integration limit can equally be chosen as $-\infty$ in order to apply the convolution theorem for Fourier transforms. When the Fourier transform of a function *h* is denoted by

$$\mathcal{F}(h)(y) = \int_{-\infty}^{\infty} h(x) e^{-ixy} dx$$
(16)

and the inverse Fourier transform by

$$\mathcal{F}^{-1}(h)(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} h(y) e^{ixy} \, dy \tag{17}$$

one obtains

$$\mathcal{F}(\chi_p)(y) = -\alpha \frac{i\pi}{\sinh \pi y} \,\mathcal{F}(\overline{v})(y),\tag{18}$$

$$\mathcal{F}(\chi_q)(y) = \alpha \frac{\pi}{\cosh \pi y} \,\mathcal{F}(\overline{v})(y). \tag{19}$$

Here, $\frac{-i\pi}{\sinh \pi y}$ and $\frac{\pi}{\cosh \pi y}$ are the Fourier transforms of the kernels K_p and K_q , respectively. Eliminating $\mathcal{F}(\overline{v})(y)$ results in the general dispersion relation

$$\mathcal{F}(\chi_q)(y) = i \tanh \pi y \, \mathcal{F}(\chi_p)(y), \tag{20}$$

which holds for arbitrary non-interacting SP particle ensembles even for mixtures of different minerals. By application of the properties of the Fourier transform and the series expansion of tanh x, this relation can be expressed in terms of derivatives as

$$\chi_q(\lambda) = \sum_{k=1}^{\infty} \frac{\pi^{2k} \, 2^{2k} \left(2^{2k} - 1\right)}{(2k)!} \, B_k \, \chi_p^{(2k-1)}(\lambda),\tag{21}$$

where B_k is the *k*th Bernoulli number. The first three terms of this expansion are

$$\chi_q(\lambda) = \pi \,\chi_p'(\lambda) + \frac{\pi^3}{3} \,\chi_p^{(3)}(\lambda) + \frac{\pi^5}{15} \chi_p^{(5)}(\lambda) + \dots$$
(22)

If the higher derivatives are negligible, we obtain Néel's approximation

$$\chi_q(\lambda) \approx \pi \, \chi_p'(\lambda). \tag{23}$$

To the best of our knowledge, only this approximative form of dispersion relation (21) has been stated before (Néel 1949; Mullins & Tite 1973; Dabas *et al.* 1992), but without discussion of the conditions for its validity. Based on (20) and (21), it can be explained why Néel's approximation in most applications performs extremely well. It only leads to errors if large wave numbers y in (20) are dominant or, equivalently, if derivatives of $\chi_p(\lambda)$ higher than the second cannot be neglected. Thus, (23) assumes smooth functions $\chi(\lambda)$ which over short intervals $\Delta\lambda \leq 1$ can be nicely approximated by quadratic functions. In terms of the effective volume distribution $\overline{v}(\epsilon)$, Néel's approximation requests a higher degree of smoothness and precludes closely spaced minima and maxima. In natural ensembles this is a weak restriction and Néel's approximation usually perfectly coincides with experimental data.

4 A SEMI-ANALYTICAL DECONVOLUTION METHOD

From both, (18) and (19) it is possible to determine $\overline{v}(\epsilon)$:

$$\overline{v}(\epsilon) = \frac{1}{\alpha \pi} \mathcal{F}^{-1}[i \sinh \pi y \, \mathcal{F}(\chi_p)(y)](\epsilon), \tag{24}$$

$$\overline{v}(\epsilon) = \frac{1}{\alpha \pi} \mathcal{F}^{-1}[\cosh \pi y \, \mathcal{F}(\chi_q)(y)](\epsilon).$$
(25)

In Néel's approximation these formulae become extremely simple, since it considers the case of small y, where sinh $\pi y \approx \pi y$ and cosh $\pi y \approx 1$. We then have from (24) and (25)

$$\overline{v}(\epsilon) = \frac{1}{\alpha} \chi'_p(\epsilon), \tag{26}$$

$$\overline{v}(\epsilon) = \frac{1}{\alpha \,\pi} \,\chi_q(\epsilon). \tag{27}$$

In other terms, Néel's approximation replaces the kernel $K_q(x)$ by Kronecker's δ -function $\pi \delta(x)$, while $K_p(x)$ is approximated by Heaviside's step function S(x) (Fig. 1). This follows directly from (15) by taking into account that $\int_{-\infty}^{\infty} \frac{d\epsilon}{2\cosh\frac{\lambda-\epsilon}{2}} = \pi$.

Eqs (24) and (25) give the exact formal solution of the inverse task of determining $\overline{v}(\epsilon)$ from FDS measurements. Their practical application is limited by two obstacles. First, a complete reconstruction of $\overline{v}(\epsilon)$ would require FDS measurement at a single temperature over about 10 frequency decades. Common measurement devices allow for at most four decades and therefore results from several temperatures must be combined into a single interpretation. Second, a direct evaluation of (24) and (25) requires numerical deconvolution. For sparse and noisy data—as they commonly occur in FDS measurements—deconvolution by discrete Fourier transform is known to produce unwanted high-frequency noise which completely spoils the signal content.

The first problem of merging FDS data from several temperatures will be the main topic of the following sections. To solve the second problem, a semi-analytical parametric deconvolution approach



Figure 1. Sketch of the kernels $K_p(\lambda - \epsilon)$ (grey) and $K_q(\lambda - \epsilon)$ (black) for a realistic value of $\epsilon = 20$. In Néel's approximation K_p is replaced by a step function, while K_q is approximated by a delta function.

is proposed where the measured values $\chi_p(\lambda_m)$ and $\chi_q(\lambda_m)$ are approximated by regularized polynomials

$$P_{\sigma}(\lambda) = \sum_{k=0}^{n} a_k \,\lambda^k \, e^{-(\lambda/\sigma)^2}, \quad Q_{\sigma}(\lambda) = \sum_{k=0}^{n} b_k \,\lambda^k \, e^{-(\lambda/\sigma)^2}.$$
(28)

The regularized monomials $\lambda^k e^{-\lambda/\sigma^2}$ are analytically deconvolved by observing that the right-hand side of both, (24) and (25), are linear combinations of expressions of the form

$$\mathcal{F}^{-1}[e^{a\,y}\,\mathcal{F}(\lambda^k\,e^{-(\lambda/\sigma)^2})(y)](x) = e^{-\left(\frac{x-ia}{\sigma}\right)^2}\,(x-ia)^k,\tag{29}$$

which are directly obtained from the Fourier integrals by substitution. For λ in a finite interval this yields in the limit $\sigma \rightarrow \infty$:

$$\mathcal{F}^{-1}\left[-i\,\sinh\pi y\,\mathcal{F}(\lambda^k)(y)\right](\epsilon) = \mathrm{Im}(x+i\pi)^k,\tag{30}$$

$$\mathcal{F}^{-1}\left[\cosh \pi y \,\mathcal{F}(\lambda^k)(y)\right](\epsilon) = \operatorname{Re}(x+i\pi)^k. \tag{31}$$

From this result, the following simple and robust deconvolution algorithm is obtained:

(1) Fit the measured values $\chi_p(\lambda_m)$ by an *n*th order polynomial $P[\lambda]$. The deconvolution of the real part is then obtained as

$$\overline{v}_{p}(\epsilon) = \frac{1}{\alpha \pi} \operatorname{Im} P(\epsilon + i\pi).$$
(32)

(2) Fit the measured values $\chi_q(\lambda_m)$ by an *n*th order polynomial $Q[\lambda]$. The deconvolution of the imaginary part is then obtained as

$$\overline{v}_q(\epsilon) = -\frac{1}{\alpha \pi} \operatorname{Re} \mathcal{Q}(\epsilon + i\pi).$$
(33)

5 INVERTING FOR VOLUME DISTRIBUTION

5.1 The general integral equation

The above results show that that only the average volume distribution $\overline{v}(\epsilon)$ can be directly derived from FDS measurements. This is in general not sufficient to determine the concentration $c(\epsilon, v)$, although $\overline{v}(\epsilon)$ and $c(\epsilon, v)$ are linked through (13) which at first glance resembles an integral equation of first kind. However, the peculiarity of this equation is that it must be solved for $c(\epsilon, v)$ and any example of two functions $c_i(\epsilon, v) = f_i(v) Y(\epsilon)$, i = 1, 2 where

$$\int_0^\infty v f_1(v) \, dv = \int_0^\infty v f_2(v) \, dv \tag{34}$$

shows, that this cannot be done in a completely general way without additional information.

5.2 Two classes of solutions

Here, two complementary cases are considered, where either some information is not required, or sufficient additional information is available to determine $c(\epsilon, v)$ with the help of (13).

(1) The concentration function $c(\epsilon, v)$ can be factorized into

$$c(\epsilon, v) = f(v) Y(\epsilon), \tag{35}$$

where $Y(\epsilon)$ is a normalized distribution function. The multiplication of (35) by v and integration yields $Y(\epsilon) = \overline{v}(\epsilon)/v_0$, where

$$v_0 = \int_0^\infty v f(v) \, dv = \int_0^\infty \overline{v}(\epsilon) \, d\epsilon \tag{36}$$

is an average volume. The right equality makes use of the fact that by definition $Y(\epsilon)$ is normalized. In this case, from the FDS experiments one can obtain the energy barrier distribution $Y(\epsilon)$ and the average volume v_0 , provided that the measured range of ϵ covers the whole distribution. However, no further features of the volume distribution f(v) can be retrieved.

(2) The concentration function $c(\epsilon, v)$ can be factorized into

$$c(\epsilon, v) = f(v) Y(\epsilon - s(v)), \tag{37}$$

where s is a strictly monotonic function and either f or Y are known. In this case, (13) transforms into the convolution integral

$$\overline{v}(\epsilon) = \int_{-\infty}^{\infty} \frac{[s^{-1}(s)]^2}{s'(s^{-1}(s))} f(s^{-1}(s)) Y(\epsilon - s) \, ds, \tag{38}$$

which can be solved for the unknown function f or Y by Fourier transform techniques.

The most simple inversion uses the assumption that $\epsilon = s(v) = \beta(T) v$, which is a special instance of the second case above. It has been used in Stephenson (1971) and Worm & Jackson (1999), where

$$\beta(T) = \frac{\mu_0 M_s(T) H_k(T)}{k_B T},$$
(39)

and microcoercivity $H_k(T)$ is due to pure shape anisotropy, $H_k(T) = \Delta N M_s(T)$ and thus independent of v. It follows that $c(\epsilon, v) = f(v) \delta(\epsilon - \beta(T)v)$ and (38) can be easily solved for the volume distribution f yielding

$$f(v) = \frac{\overline{v}(\beta(T)v)}{v}\beta(T),$$
(40)

where $\overline{v}(\beta(T)v)$ is rigorously obtained either from (32) or from (33). Less rigorously, one can apply Néel's approximation (26) or (27) to determine $\overline{v}(\beta(T)v)$ leading to

$$f(v) = \frac{\chi_q([\beta(T)v)]}{\pi v \alpha(T)} \beta(T) = 3\Delta N \frac{\chi_q[\beta(T)v]}{\pi v}$$
(41)

or

$$f(v) = 3\Delta N \, \frac{\chi'_p(\beta(T) \, v)}{v}.$$
(42)

6 APPLICATION OF THE DECONVOLUTION METHOD TO EXPERIMENTAL RESULTS

6.1 The volume distribution of Tiva Canyon tuff

We used the data sets of Worm & Jackson (1999) from Tiva Canyon tuff samples CS914, CS915, CS916 (Schlinger *et al.* 1988) to



Figure 2. Volume distributions f(v) obtained by inverting the FDS data of Tiva Canyon tuff samples CS914, CS915, CS916 (Worm & Jackson 1999; Schlinger *et al.* 1988). Each line in this plot results from inverting the FDS data at one fixed temperature. Black lines correspond to inversion of χ_p , grey lines to inversion of χ_q . At each temperature both inversions are almost indistinguishable. Grey shaded areas represent the volume distributions obtained by Worm and Jackson from SIRM as well as TRM demagnetization curves.

compare the results from our method with volume distributions of SP particles obtained by thermal demagnetization of either SIRM(5K) or TRM(5K)(Worm & Jackson 1999). It has been pointed out in Worm & Jackson (1999) that the FDS data of these samples are in good agreement with predictions based on the volume distribution inferred from thermal demagnetization curves. Our approach differs from their treatment in that we directly invert the FDS data to infer the volume distribution. Fig. 2 collects the results of all deconvolutions of FDS data at different temperatures. Each of the overlapping line segments results from deconvolution of the FDS at one fixed temperature. FDS measurements at lower temperatures only contain information about small intervals of small volumes. Hightemperature FDS measurements cover larger intervals and larger grain sizes. Due to the dense temperature steps of the measurements of Worm & Jackson (1999), volume distributions inferred from neighbouring temperatures overlap considerably. This allows to check the self-consistency of the inferred volume distribution. Fig. 2 shows, that although the general shape of the distribution is coherently outlined, there exist regions where neighbouring segments diverge in a way which is by far too systematic as to be explained by measurement error. Dark and light line segments in Fig. 2 are obtained by deconvolution of either real or imaginary parts of FDS and both coincide perfectly throughout all samples and temperatures. This indicates that the basic assumption that susceptibility variation is due to thermally activated magnetization switching processes, is correct for the Tiva Canyon samples. The order of magnitude of remaining deviations between both deconvolutions can be used to estimate the measurement error and thus confirms that divergence of neighbouring segments is real.

It is interesting to compare our inversion results with the volume distributions from Fig. 9 of Worm & Jackson (1999) and displayed

as shaded areas in Fig. 2. Although the results obtained from FDS and thermal demagnetization curves coincide quite well in general outline, the distributions from FDS have a tendency to show more fine grains. Perhaps this reflects the fact that viscous magnetization is largely eliminated from SIRM as well as TRM demagnetization curves, while it is an essential part of the FDS signal.

The most noticeable advantage of the FDS method is its ability to check the self-consistency of the volume distribution which is not achievable from thermal demagnetization curves. To make use of this additional information, it is necessary to understand and assess the possible causes of misfit. By optimizing the fit between neighbouring segments it is then possible to quantitatively estimate the influence of the distortion effects. The most obvious possible sources for systematic deviations are:

- (1) Wrong choice of τ_0 ,
- (2) Wrong choice of the function s(v),
- (3) Magnetostatic interaction.

In the remaining part of this section we discuss the first two alternatives. The much more complex question of interaction will be treated experimentally and theoretically in the next two sections.

6.1.1 Variation of τ_0

The deconvolutions of the FDS data in Fig. 2 are obtained using the constant value $\tau_0 = 10^{-9}$ s which in the sense of (8) and the subsequent discussion is the physically most reasonable estimate. Yet, Fig. 3 demonstrates for sample CS914 that decreasing τ_0 substantially improves the fit between neighbouring segments of the inversion. Optimal consistency is obtained for $\tau_0 = 10^{-13}$ s. This value, however, is utterly impossible to explain using the theoretical



Figure 3. Decreasing τ_0 from a realistic value of 10^{-9} s to a physically impossible value of 10^{-13} s improves the self-consistency of the FDS data inversion for Tiva Canyon tuff CS914.

models of either Néel (Néel 1949) or Brown (Brown 1963) as outlined in Section 2. Already the choice of γ' in (8) yielded the minimal possible value for τ_0 and in order to explain four orders of magnitude deviation between theory and experiment one would have to relinquish this theory altogether.

A closer look at Fig. 3 reveals that the improved fit for smaller values of τ_0 goes along with an increase of inferred average grain volume. This opens up another explanation of the misfit which does not require to vary τ_0 , but questions the assumed relation between energy barrier and volume.

6.1.2 Relation between volume and energy barrier

The assumed linear relation $\epsilon = \beta(T) v$ between energy barrier and volume relies on the assumption of predominant shape or crystal anisotropies. Eq. (4) elucidates that a modified relation $\epsilon = \beta v$ – ϵ_0 , where ϵ_0 is a constant, is mathematically equivalent to a reduction of τ_0 by exp $(-\epsilon_0/2)$. A very similar modification with a slightly different temperature dependence but also equivalent to a reduction of τ_0 , is given by a volume shift $\epsilon = \beta(v - v_0)$, where v_0 is a constant volume. The main problem with the above energy barrier modifications is the necessary size of $\epsilon_0 \approx 20 k_B T$ needed to reduce τ_0 by a factor of 10^{-4} as required for the best fit in Fig. 3. It is hard to imagine a physical mechanism which accounts for either such an additional perturbation energy or a corresponding reduction of the particle energy barriers. On the contrary, in very small particles additional surface anisotropy rather tends to increase the energy barrier. The discussion in Section 5 shows that much more complex relations between volume and energy barrier might be taken into account. Especially the convolution kernel Y in (38) could be a Gaussian instead of a delta-function or the functional dependency s(v) could be nonlinear, eventually reflecting a variation of H_k with volume due to incoherent magnetization reversal. Yet, it has been shown by numerical micromagnetic calculations that in magnetite SP particles incoherent magnetization reversal is of minor importance (Winklhofer et al. 1997) and it is not conceivable that a realistic distribution Y effectively decreases the energy barrier by $20k_BT$. In summary, we do not find a physical reason allowing to interpret the observed misfit by reduced τ_0 or reduced energy barrier. The apparent success of such variations in improving the fit between inversion data from different temperatures remains enigmatic.

6.2 The role of interaction: volume distribution in ferrofluids

The third possibility to account for systematic deviations of volume distributions obtained at different temperatures in the Tiva Canyon samples is magnetostatic interaction. A theoretical estimation of this effect is much more difficult than in the previous two cases since a wide variety of partly contradictory approaches exist in the literature. We therefore first performed an experimental study of the FDS for two different ferrofluid samples to check whether these interacting SP ensembles show qualitatively similar systematic misfits between inverted volume distributions obtained at different temperatures.

The commercial ferrofluid samples FF-V77 and FF-S32 have nominal average particle sizes around 3 and 10 nm, respectively, and relative volume concentration of about 1 per cent. While FF-S32 has a octane-based carrier liquid, FF-V77 is water-based. The samples were prepared by mixing them with either epoxy- or waterbased glue to obtain solid samples after drying at room temperature. Measurements of FDS were performed using the AC measurement option of the Quantum Design MPMS-XL-7T at the University of Bremen. This instrument allows for a high precision temperature control and variable AC field amplitude. All our measurement used the same amplitude of $H_{AF} = 0.4$ mT. The FDS measurement results are shown in Figs 4 and 5 in function of temperature.

Since the inversion formula for volume distribution f(v) requires a reliable estimate of $H_k(T)$ we also measured hysteresis loops at different temperatures using the MPMS-XL. The loops for sample FF-S32 are shown in Fig. 6 and yield the coercive forces $H_c(T)$ at T =10, 50 and 100 K. All loops were measured with maximum field of 3 T and the microcoercivity is obtained according to $H_k(T) =$ 2.09 $H_c(T)$ as in case of the Tiva Canyon samples (Worm & Jackson 1999).

The inversion results of the ferrofluid FDS measurements are presented in the left parts of Figs 7 and 8. Apparently the coherency between different temperatures is worse than in case of the Tiva Canyon samples since the deconvolution curves exhibit marked negative slopes even where the overall trend of the distribution function f(v) is increasing. Yet, in both types of samples the direction of the systematic misfit is the same. In the ferrofluids the negative slopes indicate that at constant temperature the FDS deconvolution systematically underestimates the volume of larger grains. While in Tiva Canyon sample CS914 the inconsistent slopes are still positive,



Figure 4. Real (left) and imaginary (right) part of the frequency-dependent susceptibility of ferrofluid FF-V77 in function of temperature. At each temperature, the susceptibility was measured at the frequencies f = 0.18, 0.34, 0.63, 0.91, 2.2, 4.0, 7.4, 13.6, 26.0, 46.4, 85.8, 158.6, 293, 542, 997 Hz. Shading varies from black (f = 0.18 Hz) to light grey (f = 997 Hz).



Figure 5. Real (left) and imaginary (right) part of the frequency-dependent susceptibility of ferrofluid FF-S32 in function of temperature. Frequencies and shading are the same as in Fig. 4.



Figure 6. Hysteresis loops of ferrofluid FF-S32 at 100 K (solid), 50 K (dashed) and 10 K (dash-dot). The maximum field of the loops in all cases was 3 T.



Figure 7. Deconvolution of FDS measurements for ferrofluid FF-S32. The left image shows the result without taking into account interaction. In the right graph, interaction is estimated by the method described in the text.

the systematic misfit also apparently underestimates the volume of larger grains. Since in ferrofluids magnetostatic interaction is definitely important, it is the most likely source of the observed misfit. Accordingly, weaker magnetostatic interaction is also a plausible explanation for the smaller misfit in the Tiva Canyon samples. We will argue below that magnetostatic interaction can explain this un-



Figure 8. Deconvolution of FDS measurements for ferrofluid FF-V77. The left image shows the result without taking into account interaction. In the right graph, interaction is estimated by the method described in the text.

derestimation and that it is even possible to determine the average interaction field by a quantitative analysis of this effect which will be given in the next section.

The presence and estimation of magnetostatic interactions is often a matter of a great concern in analyses of both, synthetic materials and natural rocks. Even though the remanence carriers in ferrofluids are carefully coated in order to prevent agglomeration due to magnetostatic interaction at room temperature, these coatings are less effective at low temperatures where interaction increases in relation to thermal energy. This is quantitatively expressed by the increase of $q(T, v) = \frac{\mu_0 H_{\text{int}} M_s(T)v}{k_B T}$, where H_{int} is the average interaction field.

At constant T, the importance of interaction as measured by q(T, v) increases with volume. Assuming that susceptibility in these samples is reduced by magnetostatic interaction, it is then possible to explain for the observed underestimation of f(v) at larger volumes in the FDS deconvolution curves at constant temperature.

The theory of interacting magnetic nanoparticle ensembles contains many difficulties and pitfalls and there is still considerable debate even about fundamental aspects. Summarizing the present state of the art, Fiorani *et al.* (1999) distinguish two regimes of weak to medium and of strong interactions. Weak or medium interactions are considered as caused by magnetic moments fluctuating in time, since interaction energy is small in comparison to k_BT . These so-called dynamic interactions increase the single particle energy barrier E_b by some interaction energy E_{int} (Dormann *et al.* 1988).

In the strong interaction regime, interaction energy dominates the thermal energy k_BT below some so-called freezing temperature $T_{\rm fr}$. In this case—similar to a spin glass—the whole system forms a collective phase and the interaction fields are constant in time. This idea, already suggested in Shcherbakov & Shcherbakova (1977), has been developed by a number of authors (Dormann *et al.* 1988; Fiorani *et al.* 1999; Muxworthy 2001; Ulrich *et al.* 2003). The similarity between spin-glasses and interacting particle ensembles has its physical reason in the random direction and value of the dipole–dipole interactions due to the random mutual position of the grains. This closely resembles the random RKKY couplings between the atoms in a spin-glass. The random particle distribution causes random interaction fields H_{int} acting along the easy axes of the grains which is just the pre-condition for the spin-glass transition.

Whilst a detailed scrutiny of the problem of interacting magnetic nanoparticles is far beyond the scope of this article, we do need a simple method to account for the effect of interactions during the FDS deconvolution. In the next section, we develop a new theoretical approach to calculate a mean field (MF) interaction correction for the deconvolution problem. This allows to estimate the interaction strength from our FDS measurements and also yields an improved estimate for the actual particle volume distribution f(v) which is not biased by static interaction fields. These corrected distributions are already displayed on the right-hand side of Figs 7 and 8.

7 MEAN FIELD CORRECTION FOR MAGNETOSTATIC INTERACTIONS

Muxworthy recently considered the effect of weak or moderate dipolar interaction on the FDS, accounting primarily for influence of interactions upon blocking volume (Muxworthy 2001). Here, however, we have to deal with the case of interactions strong enough to substantially disturb the reconstruction of the volume distribution f(v) using (40). Such strong interaction fields are either due to a particle volume distribution allowing for large grains to be already frozen while sufficiently many small particles still have short relaxation times, or due to freezing of a collective state, which essentially has the same effect since a prominent feature of collective states also is a critical reduction of the collective relaxation time (Fiorani et al. 1999; Ulrich et al. 2003). We treat this problem of strong interactions by an MF approximation. Dynamic interactions between unblocked particles, which usually are regarded as principal interaction effect (Dormann et al. 1988; Muxworthy 2001), can be included in our approach, but turn out to be negligible in first order. On the other hand, average static interaction turns out to be significant. In our MF approximation it emerges by a second-order phase transition below a freezing temperature $T_{\rm fr}$. Since the average interaction field in this case increases with decreasing temperature proportional to $\sqrt{1 - T/T_{\rm fr}}$, the normalized distribution function $W(H_{int}, T)$ of interaction fields H_{int} accordingly transforms as

$$W(H_{\rm int}, T) \propto W(H_{\rm int}/\sqrt{1 - T/T_{\rm fr}}, 0).$$
 (43)

In accordance with the MF concept, the total magnetic field at a single particles' position is considered as the sum of external and interaction fields $H = H_e + H_{int}$. In our case of susceptibility measurements in strongly interacting ensembles we assume that $H_e \ll H_{int} \ll H_k$ and after normalization to H_k we get $h = h_{int} + h_e$, where $h_e = H_e/H_k \ll h_{int} = H_{int}/H_k \ll 1$.

Following Néel (Néel 1949), we describe the magnetic relaxation process of a single particle as a dynamic equilibration between two inversely magnetized states as sketched in Fig. 9.

The master equation for the probability x of the system being in state 1 is

$$\frac{dx}{dt} = -\frac{x}{\tau_1} + \frac{1-x}{\tau_2},$$
(44)



Figure 9. Relaxation process in a two-state system with energy barrier. The transition from state 1 with population density *x* to state 2 has a relaxation time of τ_1 . Correspondingly, the transition from state 2 with population density 1 - x to state 1 has relaxation time τ_2 .

where τ_1 is the relaxation time of the process $1 \rightarrow 2$ and τ_2 is the relaxation time of the process $2 \rightarrow 1$. Since the states are inversely magnetized, the total magnetization is given by m = 2x - 1 and the master equation (44) implies the magnetization dynamics

$$\frac{dm}{dt} = -m \left[\frac{1}{\tau_1} + \frac{1}{\tau_2} \right] + \left[\frac{1}{\tau_2} - \frac{1}{\tau_1} \right].$$
(45)

Néel and Brown (Néel 1949; Brown 1959, 1963) calculated the relaxation times $\tau_{1,2}$ using different physical approaches, but obtained nearly identical results. Néel's expression is given by

$$\tau_{1,2} = \tau_0 \, \exp\left[\frac{\beta v}{2} \, (1\pm h)^2\right] = \tau_0 \, \exp\left[\frac{\beta v}{2} \, (1+h^2)\right] \exp(\pm\beta vh).$$
(46)

Inserting this into (45) results in

$$\tau \, \frac{dm}{dt} + m = \tanh\left[\beta vh\right],\tag{47}$$

where $\tau = \tau_0 \exp[\frac{\beta v}{2} (1 + h^2)] / \cosh[\beta v h]$.

Even though we assume $h_{\text{int}} \ll 1$, this doesn't imply that also $\beta v h_{\text{int}} \ll 1$. On the contrary, freezing of collective states at T_{fr} rather requires $\beta v h_{\text{int}} \approx 1$ which demands $\beta v \gg 1$ for $T < T_{\text{fr}}$. However, to finally obtain a relatively simple expression for χ which preserves the basic properties of (11), we restrict ourselves to cases where $\beta v h_{\text{int}}^2 \ll 1$ as well as $\beta v h_e \ll 1$. Then, eq. (47) can be rewritten as

$$\tau \left[1 - \beta v \tanh(\beta v h_{\text{int}}) h_{\text{e}}\right] \frac{dm}{dt} + m$$

= $\tanh \left[\beta v h_{\text{int}}\right] + \beta v \operatorname{sech}^{2} \left[\beta v h_{\text{int}}\right] h_{\text{e}}$ (48)

where now $\tau = \tau_0 \exp[\frac{\beta v}{2}]/\cosh[\beta v h_{\text{int}}]$.

In our MF approach we neglect correlations between interacting particles and assume equal probability for the interaction field h_{int} to be directed at either direction along the particles' easy axis. Therefore, $W(h_{\text{int}})$ is a symmetric distribution function with zero average interaction field. We denote an average of a quantity Q over $W(h_{\text{int}})$ by

$$\langle Q \rangle = \int_{-\infty}^{\infty} Q W(h_{\text{int}}) dh_{\text{int}}, \qquad (49)$$

and thus write the average of eq. (48) over $W(h_{int})$ as

$$\langle \tau \rangle \frac{dm}{dt} + m = \beta v \langle \operatorname{sech}^2 [\beta v h_{\operatorname{int}}] \rangle h_{\mathrm{e}},$$
(50)

where

$$\langle \tau \rangle = \tau_0 \exp\left[\frac{\beta v}{2}\right] \langle \operatorname{sech} [\beta v h_{\operatorname{int}}] \rangle.$$
 (51)

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Figure 10. A sufficiently strong static interaction field $H_{\text{int}} \gg H_{\text{ext}}$ decreases the measured susceptibility χ_{int} with respect to the initial susceptibility χ_0 by shifting the working point in the nonlinear part of the anhysteretic curve.

In case of a time-variable external field $h_e(t) = h_e e^{i\omega t}$, one obtains in analogy to (10) the complex susceptibility

$$\chi(\omega, \tau) = \frac{\chi_0 \left\langle \operatorname{sech}^2 \left[\beta v h_{\operatorname{int}}\right] \right\rangle}{1 + i \,\omega \left\langle \tau \right\rangle}.$$
(52)

This equation shows that the primary effect of static interaction is a diminution of susceptibility by the factor $(\operatorname{sech}^2[\beta vh_{int}])$. As expected, this reduction increases exponentially with increasing volume. Fig. 10 illustrates that the mechanism of susceptibility reduction by interaction in the regime defined by our above assumptions is that due to the large static interaction field the small AC field is working in the nonlinear part of the anhysteretic magnetization curve.

We now further simplify (52) by setting for T = 0 K

$$W(h_{\rm int}) = \frac{1}{2} \left[\delta(h_{\rm int} + h_0) + \delta(h_{\rm int} - h_0) \right], \tag{53}$$

which essentially replaces $(\operatorname{sech}^2(\beta v h_{\operatorname{int}}))$ with $\operatorname{sech}^2(\beta v h_0)$ for some characteristic static interaction field h_0 . The temperaturedependent $h_0(T)$ is then given by

$$h_0(T) = h_0 \sqrt{1 - \frac{T}{T_{\rm fr}}}.$$
(54)

A second static interaction effect upon susceptibility in (52) is the deviation of relaxation time $\langle \tau \rangle$, given by (51), from τ as used in the previous sections. This deviation is an average decrease by $(\operatorname{sech}(\beta v h_{int}))$ which we further simplify by replacing $\cosh(x)$ with $\exp(x)$ for positive arguments. The resulting error in $\langle \tau \rangle$ is less than a factor of 2 which is negligible in comparison to the uncertainties in τ_0 . In contrast, the correction itself varies between $\beta v h_{int} \ll 1$ and $\beta v h_{int} > 3$ by an order of magnitude. Since h_{int} here refers to a static interaction field, its influence upon $\langle \tau \rangle$ compares to the Mørup–Tronc model of interaction in magnetic nanoparticles (Mørup & Tronc 1994; Hansen & Mørup 1998). Dynamic interactions also can be taken into account by an additional dynamic energy barrier ϵ_{int} ($\alpha(T)v$) in units of kT which in analogy to Dormann *et al.* (1998) results in a modified Brown formula

$$\langle \tau \rangle = \tau_0 \, \exp\left[\frac{(\beta v + \epsilon_{\rm int}(\alpha v))(1 - 2h_0)}{2}\right].$$
(55)

Even this more involved representation of $\langle \tau \rangle$ still allows to interpret χ in terms of a convolution similar to (15). Whilst the relaxation time is reduced by static interactions, dynamic interactions according to Dormann *et al.* (1988) and Muxworthy (2001) increase it and to some extent both effects may cancel each other. In any case, our calculations persistently show that the correction of $\langle \tau \rangle$ is only a minor contribution in comparison to susceptibility reduction by

sech²(βvh_0). Therefore, in the following, we consider only the static interaction field by setting $\epsilon_{int}(\alpha v) = 0$.

It is possible to estimate typical values for the static interaction field h_0 by considering a dipole–dipole interaction field between nearest neighbours. When r_{nn} denotes the average distance between nearest neighbours and v_{av} is the average particle volume,

$$h_0 \simeq \frac{M_{\rm s} \, v_{\rm av}}{r_{\rm nn}^3 \, H_{\rm k}}.$$
 (56)

Since for equi-distributed grains the concentration *c* is approximately $c \approx \frac{v_{\text{av}}}{r_{\text{nn}}^3}$ we obtain $h_0 \approx M_{\text{s}} c / H_{\text{k}}$. Further simplification using the approximation $H_k = \Delta N M_{\text{s}}$, where ΔN is the demagnetizing factor, results in the final estimate

$$h_0 \approx c/\Delta N.$$
 (57)

Thus, for plausible values of 0.005 < c < 0.1 we obtain $0.02 < h_0 < 0.1$. Values of h_0 in this range are completely sufficient to get a substantial decrease in χ for our typical energy barriers of $\epsilon = \beta v \in [10, 50]$.

In analogy to (12) integrating (52) over all volumes and energy barriers yields the ensemble's complex susceptibility

$$\chi(\omega, T) = \alpha \operatorname{sech}^{2} \left[\beta v h_{0}\right] \int_{0}^{\infty} \int_{0}^{\infty} \frac{v c(\epsilon, v)}{1 + i \omega \tau_{0} \exp\left[\beta v \left(\frac{1}{2} - h_{0}\right)\right]} dv d\epsilon.$$
(58)

Taking into account the changes between (12) and (58), the inversion by formula (40) can be rewritten as

$$f(v) = \frac{\overline{v}[\beta v (1 - 2h_0)]}{v} \cosh^2[\beta v h_0] \beta.$$
(59)

7.1 Application of the interaction correction

In practical applications of the described method, it is necessary to choose reasonable values for the interaction parameters h_0 and T_{fr} .

While the freezing temperature $T_{\rm fr}$ could be estimated by the temperature where $\chi(\omega, T)$ for lowest ω reaches its maximum (Dormann *et al.* 1988), the choice of an *a priori* h_0 is not equally simple because the inversion crucially depends on the accuracy of this value and (57) is by far too inexact. However, the inversion of our data itself allows to judge the quality of an estimate for $T_{\rm fr}$ and h_0 , since for a correct choice, the inversions at different temperatures should result in a continuous self-overlapping volume distribution.

A simple measure for the continuity of the inversions from two adjacent temperatures is the square distance of the centre values in their overlapping volume range. By minimizing the sum $S(h_0, T_{\rm fr})$ over all these squares, one obtains an intrinsic estimate of $T_{\rm fr}$ and h_0 .

This method has been used to determine T_{fr} and h_0 for the ferrofluid samples FF-S32 and FF-V77.

After correction according to (59), the optimally self-consistent particle volume distributions shown on the right hand side of Figs 7 and 8 are obtained. Applying the same correction methods to the Tiva Canyon tuff samples also decreases the misfit and creates the more smooth volume distributions presented in Fig. 11. The corresponding values for $T_{\rm fr}$ and h_0 are collected in Table 1.

8 SUMMARY AND DISCUSSION

The initial idea of this study was to provide a rigorous theoretical background for the determination of volume and coercivity distribution of an SP particle ensemble from FDS measurements at



Figure 11. Deconvolution of the FDS data of Tiva Canyon tuff (Worm & Jackson 1999), taking into account the effect of interaction. Interaction field and freezing temperature have been determined by minimizing the overlap between adjacent measurement curves.

Table 1. Optimal fit of freezing temperature $T_{\rm fr}$ and relative interaction field h_0 obtained by minimizing the sum $S(h_0, T_{\rm fr})$ over all measured temperatures. This minimizes the misfit between adjacent temperature inversions for the volume distribution according to (59).

Sample	$T_{\rm fr}[{ m K}]$	h_0 [per cent]	$H_{\text{int}}(0 K) [\text{mT}]$
FF-S32	133	2.4	1.0
FF-V77	18.3	3.0	1.0
CS914	352	2.2	2.0
CS915	186	1.6	2.1
CS916	92	0.7	0.7

different temperatures. We have shown that this problem is ill-posed and cannot be solved generally. Yet, by a combination of convolution and deconvolution methods it is possible to uniquely determine the effective volume $\overline{v}(\epsilon)$ of particles with energy barrier ϵ . When an additional relation between volume and ϵ is assumed, it is then possible to infer the volume distribution. The generally valid relations between susceptibility and $\overline{v}(\epsilon)$ are easily evaluated in practical applications since the respective numerical routine requires only a polynomial representation of the measured susceptibility to obtain the energy barrier distribution.

In case of ideal SP ensembles, both eqs (32) and (33) yield the same $\overline{v}(\epsilon)$ and any significant deviation between the two indicates that the frequency dependence may result from other physical mechanisms than superparamagnetism. The coincidence of both results in SP ensembles is due to the general dispersion relation (20) between the Fourier transforms of real and imaginary parts of the susceptibility. In the limit of small wave numbers this relation becomes Néel's dispersion relation (23) between real and imaginary part of complex susceptibility. Although Néel's relation is widely used, to our knowledge this is the first study of the pre-conditions of its validity. In physical terms, the limit of small wave numbers is equivalent to the requirement that susceptibility varies smoothly and slowly with the logarithm of frequency such that it can be sufficiently well approximated by a quadratic function. Néel's dispersion relation approximates the real part of each single grain's susceptibility by a step function on the logarithmic frequency scale. Correspondingly, the imaginary part of susceptibility is estimated by a delta-function. This difference in response also explains for the substantially lower values of the imaginary part with respect to the real part of susceptibility. Only in the case of very sharp grain-size distributions where the available range of relaxation times is restricted to about one decade, real and imaginary susceptibilities can be of the same order.

As stated above, a main result of our analysis is that the concentration function $c(\epsilon, v)$ cannot be recovered unconditionally from FDS data and that only the effective volume $\overline{v}(\epsilon)$ in function of energy barrier ϵ is uniquely determined by (13) without imposing additional restrictions on $c(\epsilon, v)$. This results from the general structure of the basic integral equation (12), since its kernel depends on ϵ only, and is independent of v. Nevertheless, by using the approximative relation $\epsilon = \beta(T)v$ one obtains an estimate of the volume distribution f(v) which in case of the Tiva Canyon tuff samples resulted in relatively consistent inversion curves from different temperatures which also coincide well with previous results obtained on these samples (Worm & Jackson 1999).

However, a remaining systematic misfit led us to the study of synthetic ferrofluid samples exhibiting a much more substantial misfit between inversion curves, obtained for different temperatures. We attribute this misfit to the prevailing role of magnetostatic interactions in these samples.

In order to remove the inconsistency, we propose a new and robust method to correct for static interaction in magnetic nanoparticle ensembles. Besides resulting in a much more self-consistent volume distribution, the new correction method yields estimates for interaction field and freezing temperature. In all studied cases the inferred interaction fields lie between 0.5 and 3 per cent of H_k or between 0.5 and 2.1 mT at T = 0 K which appear to be reasonable estimates. The interaction correction also noticeably reduces the small systematic misfit, which has been observed in the initial inversion of the Tiva Canyon tuff samples.

It is interesting to compare the results of the interaction correction to that obtained by varying τ_0 (Fig. 3). Although in both cases an improved fit is achieved, the τ_0 -method substantially increases average volume in comparison to the interaction correction in Fig. 11. This volume shift sheds light on a fundamental difference between the two corrections. While variation of τ_0 essentially stretches the volume axis, the interaction correction rather expands the susceptibility axis due to the suppression of FDS by static interactions, especially at low temperature.

Summarizing, we believe that the determination of the volume distribution spectrum by means of detailed measurements of FDS at a set of low and high temperatures can provide substantially more precise information about the sizes of fine magnetic grains in rocks, sediments and soils than traditional measurements of hysteresis parameters and thermomagnetic curves.

ACKNOWLEDGMENTS

We thank H.-U. Worm and M. Jackson for kindly providing the original measurement data of the Tiva Canyon samples. Helpful

remarks by C. Constable and an anonymous referee are gratefully acknowledged. This research was made possible by a 2-month stay of VS at the University of Bremen as guest professor of the SFB 261 and by support from DFG grants BL154/24 and Fa408/2.

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