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Domain state stabilization by iterated thermal magnetization processes

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SUMMARY

Repeated heating and cooling cycles appear frequently in thermomagnetic experiments used to infer the palaeomagnetic field intensity. According to the fundamental assumptions used to interpret these measurements, a remanence acquired at some temperature T is not influenced by subsequent heating and cooling cycles at lower temperatures. This presumption is tested for natural and synthetic multidomain particle ensembles in the case of the so-called tail of pTRM* (partial thermoremanent magnetization). This case is of special interest, since hitherto no theoretical explanation for the tail of pTRM* has been available. The experimental results for all samples show that repeating the acquisition process for the tail of pTRM* leads to an asymptotic saturation. This phenomenon can be explained in terms of a statistical theory of multidomain thermoremanence based on concepts of non-equilibrium thermodynamics. The presented experiments support the hypothesis that domain state stabilization by iterated thermal magnetization processes in multidomain particle ensembles is a statistical process. Iterative saturation of the tail of pTRM* can be interpreted using a combination of exponential saturation functions related to the subspectrum of the involved transition matrix. Its explanation does not require chemical alteration or irreversible after-effects.

Key words: rock magnetism, stochastic matrix, thermoremanent magnetization.

1 INTRODUCTION

Several theoretical models have been proposed to describe the physical process by which large multidomain particles acquire thermoremanent magnetization (TRM). Prior to the articles of McClelland & Sugiura (1987) and Shcherbakov *et al.* (1993) theoretical approaches to this problem were based on the two-domain hysteretic TRM model of Néel (1955). McClelland & Sugiura (1987) and Shcherbakov *et al.* (1993) use the analogy between multidomain (MD) remanence and spin glasses to postulate a master equation for the remanence as a function of temperature. This established a first link between MD remanence and non-equilibrium thermodynamics which became increasingly important. The most convincing experimental evidence of the statistical nature of MD thermoremanence is the microscopic observation of many different domain states within the same particle after repeated identical TRM acquisition processes (Halgedahl 1991). This observation has been interpreted by directly applying renormalization group theory to the ferromagnetic ordering process in the vicinity of the Curie temperature T_C (Ye & Merrill 1995). This was the next big step towards a non-equilibrium thermodynamic interpretation, although it did not take into account changes of domain structure below T_C. That such changes occur is demonstrated by a large amount of experimental evidence, reviewed in Shcherbakov *et al.* (1993). As an extension of Thellier's law of additivity, astonishing relations between MD magnetization processes have been discovered (Shcherbakova *et al.* 2000; Dunlop & Ozdemir 2001). Phenomenological models have been proposed to understand why such relations can hold even for highly irregular MD particle ensembles (Shcherbakova *et al.* 2000; Fabian 2000). They deduce the observed relations from simple mathematical models, but have no firm physical basis. The need for a better understanding of the influence of MD particles upon the Thellier experiment for determination of the absolute palaeointensity led to increased interest in the properties of MD TRM during repeated heating and cooling. MD samples violate Thellier's law of independence. Therefore, repeated heating and cooling produces spurious remanences which are difficult to understand and to account for in palaeointensity studies. The simplest remanence of this type is the tail of partial TRM (pTRM). This was discovered by Shashkanov & Metallova (1972) and extensively studied by Shcherbakov *et al.* (1993)and Shcherbakova *et al.* (2000). However, it turned out that a slightly different spurious remanence, the tail of pTRM* (tpTRM*) (Shcherbakov *et al.* 1993), poses even more difficulties for the interpretation of palaeointensity measurements (Fabian 2001).

The present study focuses on the physical properties of iterated thermal processes and here especially on tpTRM*. A pTRM* is generated by first cooling a sample in zero field to room temperature T_0 and then heating it to some temperature $T_1 < T_C$. Afterwards a weak external field H is switched on and the sample is cooled in the field to T_0. This pTRM* is usually smaller than the

corresponding full pTRM which is acquired by cooling from T_C to T_1, switching on the field H and then cooling to T_0 (Shcherbakov *et al.* 1993; Shcherbakova *et al.* 2000). The tail of pTRM* is the residual remanence left after again heating the pTRM* to T_1 and then cooling in zero field. Its practical importance arises from the fact that the classical experiments for palaeointensity determination (Thellier & Thellier 1959; Coe 1967) rely on many repetitive heating and cooling steps and generate a sequence of tpTRM*s which may partly overprint the original NRM. A recent study by Biggin & Böhnel (2003) explicitly investigates the effects of repeated heating. To correctly interpret the results of these experiments, a theoretical understanding of tpTRM* is indispensable.

When Thellier's law of independence is valid, no tpTRM* exists. Yet, in MD samples considerable tpTRM*s are frequently observed. The existence of a tpTRM* is intuitively attributed to changes in blocking and unblocking spectra of the particle ensemble during thermal treatment. This could suggest that irreversible effects, like chemical alteration, or irreversible changes of the defect structure might be responsible for tpTRM*. However, hitherto there has been no physical model of this phenomenon.

Here, a statistical MD TRM theory (Fabian 2003) is applied to understand the variation of remanence during iterated tpTRM* acquisition processes. The predictions from this theory are compared with the results of experimental investigations on several natural and synthetic MD samples.

2 A STATISTICAL THEORY OF ITERATED THERMAL PROCESSES

The statistical theory of MD TRM (Fabian 2003) applied here assumes that a sample can adopt different *irreversible* states S_i, $i \in \{-N, \ldots, N\}$. For each state S_i, the antisymmetric state $S_{-i} = -S_i$ is obtained by inversion of the magnetization structure of S_i. The state $S_0 = -S_0$ is defined to denote the non-ordered paramagnetic state at $T \geq T_C$. The irreversible state of the sample uniquely determines the domain state of each particle up to reversible variations such as reversible domain wall bowing or reversible spin rotations. When a single particle is considered (which is not usually recommended for a statistical theory) the irreversible states correspond to all possible domain states (Fig. 1), at no matter which temperature they can occur.

The magnetic state of the ensemble is described by a ket vector: the probability distribution $|\rho\rangle$ over all possible irreversible magnetization states. The ith component $|\rho\rangle_i$, $i \in \{-N, \ldots, N\}$ of this distribution denotes the probability of the ensemble to be in state S_i. Therefore, $|\rho\rangle_i \geq 0$ and the sum over all $|\rho\rangle_i$ is 1. For given temperature T and external field H it is possible to assign to each state S_i its remanence $m(S_i)$. The bra vector $\langle m|$ collects all $m(S_i)$ into an operator which, when applied to a probability density ket $|\rho\rangle$, yields the measured remanence $\langle m|\rho\rangle$.

A central concept of statistical theory is *point symmetry*. A quantity is *point symmetric* if it remains unchanged by inversion of all spins, it is *point antisymmetric* if it changes sign by inversion of all spins. For example, the relation $m(S_{-i}) = -m(S_i)$ for the remanence of inverse states implies that $\langle m|$ is *point antisymmetric*. On the other hand, after cooling of an MD ensemble from T_C in zero field, the probability of inverse states S_i and S_{-i} is equal. Consequently, the final probability distribution $|\rho\rangle$ is *point symmetric*. Both properties together yield that the measured remanence $\langle m|\rho\rangle$ is zero.

A thermal magnetization process P is represented by its transition matrix $\mathbf{M}(P)$ acting upon the probability distribution $|\rho\rangle$. The matrix component M_{ij} is the probability that during the process P the initial state S_j is transformed into the final state S_i. The new probability density $|\rho_{\text{new}}\rangle$ after the process is obtained by

$$|\rho_{\text{new}}\rangle = \mathbf{M}(P)|\rho\rangle. \tag{1}$$

The sum of all $|\rho_{\text{new}}\rangle_i$ again must be 1. This requires that $\mathbf{M}(P)$ is a stochastic matrix, i.e. that $\sum_i M_{ij} = 1$. In realistic cases, calculating or measuring all entries of the matrix $\mathbf{M}(P)$ would be very hard or even impossible. Fortunately, several properties of thermoremanence do not depend upon details of $\mathbf{M}(P)$. For example, linearity and additivity of pTRMs can be inferred from general physical principles and symmetry considerations (Fabian 2003).

A magnetization process P is *iterative* if both temperature T and field H are the same before and after the process. This implies that the process can be performed repetitively leading to a sequence of processes $P, P^2, \ldots, P^k$. The process P^k is the kth iteration of P and accordingly its transition matrix is given by

$$\mathbf{M}(P^k) = \mathbf{M}(P)^k. \tag{2}$$

Since the matrix $\mathbf{M}(P)$ is *stochastic*, it is possible to predict how the sequence of probability densities $|\rho^{(k)}\rangle = \mathbf{M}(P^k)|\rho^{(0)}\rangle$ develops. According to the theorem of Frobenius and Perron a stochastic matrix has the principal eigenvalue $\lambda_{\text{FP}} = 1$ with a corresponding probability density eigenvector $|\rho^{\infty}\rangle$. For all other eigenvalues $\lambda_{(j)}$ the modulus $|\lambda_{(j)}|$ is less than 1 and the sum of the components of their eigenvectors $|\gamma^{(j)}\rangle$ is zero (see appendix). As a consequence, the initial state $|\rho^{(0)}\rangle$ of the iterative process can always be decomposed with respect to the eigensystem of $\mathbf{M}(P)$ as

$$\left|\rho^{(0)}\right\rangle = |\rho^{\infty}\rangle + \sum_{j=2}^{K} a^{(j)}\left|\gamma^{(j)}\right\rangle, \tag{3}$$

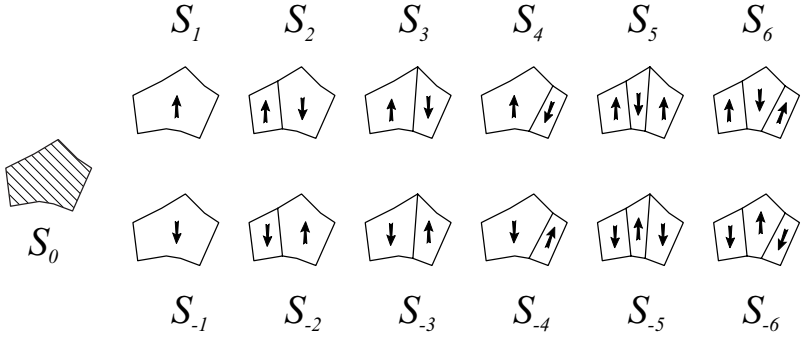

Figure 1. Simplified example of a collection of irreversible magnetization states within a single MD particle.

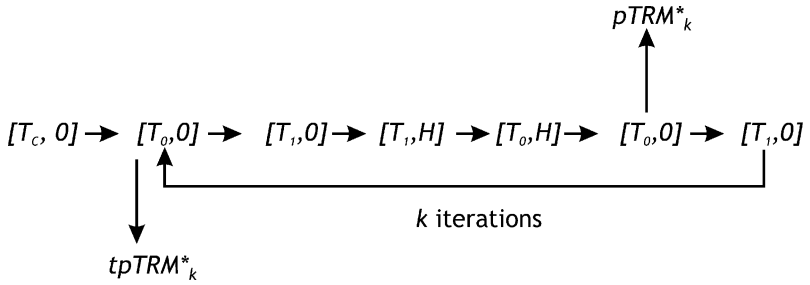

Figure 2. Experimental procedure for iterative acquisition of pTRM_k^* and tpTRM_k^*.

where the $a^{(j)}$ are real numbers. From this decomposition it follows that after k iterations the probability density is

$$\left|\rho^{(k)}\right\rangle = \mathbf{M}^k\left|\rho^{(0)}\right\rangle = |\rho^{\infty}\rangle + \sum_{j=2}^{K} a^{(j)}\lambda_{(j)}^k\left|\gamma^{(j)}\right\rangle. \tag{4}$$

Contributions from the eigenvectors $|\gamma^{(j)}\rangle$ with eigenvalues of norm <1 exponentially decay away. In the limit $k \to \infty$ the probability distribution stabilizes at $|\rho^{\infty}\rangle$. The sample remanence after k iterations is

$$m^{(k)} = \left\langle m|\rho^{(k)}\right\rangle = \langle m|\rho^{\infty}\rangle + \sum_{j=2}^{K}\lambda_{(j)}^k\left\langle m|a^{(j)}\gamma^{(j)}\right\rangle, \tag{5}$$

and also stabilizes at a limit value $m^{\infty} = \langle m|\rho^{\infty}\rangle$.

Fig. 2 schematically shows the iterative process of tpTRM_k^* acquisition. Its initial position is $Z = [T_0, 0]$ indicating room temperature T_0 and external field $H = 0$. The initial probability distribution $|\rho^{(0)}\rangle$ is obtained by zero-field cooling from the Curie temperature T_C. Since no field is applied during cooling, this distribution is point symmetric and the initial remanence $\langle m|\rho^{(0)}\rangle$ is zero. After the first tpTRM* acquisition process P, the sample's state is

$$\left|\rho^{(1)}\right\rangle = \mathbf{M}(P)\left|\rho^{(0)}\right\rangle. \tag{6}$$

During the first cooling part of the process P a weak field is applied. This destroys the initial point symmetry of $|\rho^{(0)}\rangle$ (Fabian 2003). Further thermal processes in zero field do not completely restore point symmetry—even though they tend to do this. Consequently, the finally obtained distribution $|\rho^{(1)}\rangle$ is not point symmetric and the sample potentially carries a remanence because $\langle m|\rho^{(1)}\rangle$ is not zero by symmetry anymore. This residual remanence is the observed tpTRM_1^*.

The previous argument can be stated more formally by splitting the tpTRM* acquisition process into two processes: field cycling $P_H = [T_0, 0] \to [T_1, 0] \to [T_1, H] \to [T_0, H] \to [T_0, 0]$ and subsequent zero-field cycling $P_0 = [T_0, 0] \to [T_1, 0] \to [T_0, 0]$. Thus, $P = P_H \to P_0$ and consequently the transition matrix $\mathbf{M} = \mathbf{M}(P)$ is the product of the transition matrices $\mathbf{M}_0 = \mathbf{M}(P_0)$ and $\mathbf{M}_H = \mathbf{M}(P_H)$. For weak fields H, $\mathbf{M}_H$ deviates from $\mathbf{M}_0$ only by a small perturbation and can be linearly expanded as $\mathbf{M}_H = \mathbf{M}_0 + H\,\mathbf{R}$, where $\mathbf{R}$ is point antisymmetric (Fabian 2003). $\mathbf{M}_0$ as a zero-field transition matrix is point symmetric. Combining these results yields for $\mathbf{M}$ the decomposition

$$\mathbf{M} = \mathbf{M}_0\mathbf{M}_H \approx \mathbf{M}_0^2 + H\mathbf{M}_0\mathbf{R}. \tag{7}$$

Accordingly, the first-order expansion of the kth iteration $\mathbf{M}^k$ is given by

$$\mathbf{M}^k \approx \mathbf{M}_0^{2k} + H\sum_{i=1}^{k}\mathbf{M}_0^{2i-1}\mathbf{R}\mathbf{M}_0^{2(k-i)}. \tag{8}$$

To hypothesize about the remanence behaviour, let us assume for a moment that, approximately,

$$\left|\rho^{(0)}\right\rangle = \mathbf{M}_0^2\left|\rho^{(0)}\right\rangle, \tag{9}$$

meaning that zero-field heating and cooling do not change the initial probability distribution. However, there exists experimental evidence that this *ad hoc* assumption is violated in the case of pTRM_b and pTRM_b^* studied by Shcherbakov & Shcherbakova (2001) and it will not be used in the more detailed discussion of the next sections. Using the assumption (9), the remanence change from step k to $k+1$ is

$$m^{(k+1)} - m^{(k)} = H\left\langle m\left|\mathbf{M}_0^{2k+1}\mathbf{R}\right|\rho^{(0)}\right\rangle. \tag{10}$$

As in (5), it can be inferred that remanence will relax to some limit value. In addition, for a physically plausible zero-field cycling matrix $\mathbf{M}_0$ the absolute value of $m^{(k)}$ increases steadily.

In the next section it will be tested whether the evolution according to eqs (5) and (10) is consistent with experimental data.

3 EXPERIMENTAL METHOD

The experiments have been performed on six multidomain samples. Four natural samples (6b, 12b, 11b, 1109) are Tasmanian dolerites and have been magnetically characterized in Shcherbakova *et al.* (2000). The mineralogy and ferromagnetic components of these samples are described in Schmidt & McDougall (1977). Two synthetic samples (B and JM-1) are highly oxidized magnetite after thermal stabilization for more than 1 h at $T > 700^{\circ}$C in air.

The common magnetic characteristics of the natural samples are presented in Shcherbakova *et al.* (2000). They encompass T_C, reduced saturation remanence M_{rs}/M_s, coercive force H_c, remanent coercive force H_{cr}, and the Königsberger ratio $Q_t = \chi_{TRM}/\chi_0$. Here χ_0 is the magnetic initial susceptibility and χ_{TRM} is the susceptibility of thermoremanence acquisition, approximated by $\mathrm{TRM}(H)/H$ for weak fields. Moreover, pTRM spectra and values of $\mathrm{pTRM}(T_1, T_2)$ and $\mathrm{pTRM}^*(T_1, T_2)$ imparted at different temperature intervals are given in Shcherbakova *et al.* (2000).

All experiments have been performed using the induction coil thermomagnetometer described in (Shcherbakova *et al.* 2000). The device continuously measures the magnetic moment of a rotating sample during a prescribed series of temperature cycles. Here, the temperature cycles are set to iteratively produce and delete a $\mathrm{pTRM}^*(T_0, T_1)$ between room temperature T_0 and an upper temperature T_1, either set to 300 or 400 °C. Since all measurement cycles are computer controlled, heating and cooling rates are exactly reproducible. Remanent magnetization is monitored and continuously recorded by a PC. The noise threshold of the magnetometer is 3×10^{-9} A m^2 for a cubic sample with 1 cm edge length. The

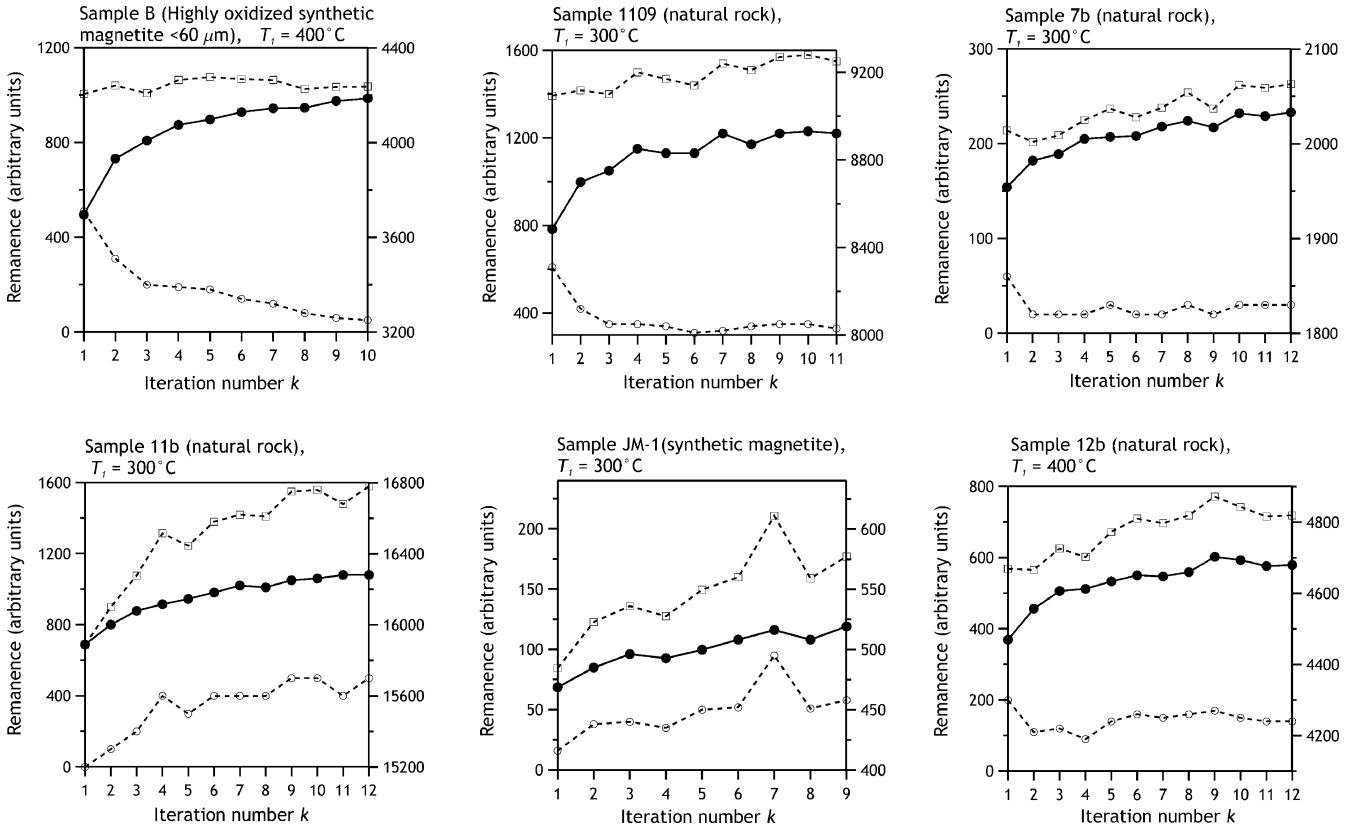

Figure 3. Experimental results for six MD samples. The left-hand axis indicates relative values of tpTRM_k^* (full circles, solid lines), whereas the relative values of pTRM_k^* (circles, dashed lines) and $\mathrm{pTRM}_k^* + \mathrm{tpTRM}_k^*$ (squares, dashed lines) are given by the right-hand axis.

maximum available external field is 200 μT, while the residual field, after switching off the coil, is less than 0.1 μT.

4 EXPERIMENTAL RESULTS

Between nine and 12 heating and cooling cycles according to Fig. 2 have been performed for each of the six samples. The results in Fig. 3 show that all samples behave very similarly with respect to tpTRM_k^* acquisition. In all cases, the values of tpTRM_k^* increase rapidly in the first step from the thermally demagnetized state at $k = 0$, where $\mathrm{pTRM}_k^* = \mathrm{tpTRM}_k^* = 0$ to $k = 1$. During the following steps from $k = 1$ to higher k values the continuous increase of tpTRM_k^* resembles an exponential approach to a limit value and is very well described by the phenomenological equation

$$\mathrm{tpTRM}_k^*/\mathrm{tpTRM}_1^* = a - b\lambda^k. \tag{11}$$

The best least-squares fit values for a, b and λ are given in Table 1. These fits do not extend to $k = 0$ where the measured remanence is exactly zero instead of $a - b$. It is not possible to find any reasonable exponential fit of the data which includes the zero-remanence point at $k = 0$. Moreover, the values of λ are relatively high, indicating a slow approach to saturation. These facts will be the starting point of the physical discussion in the next section. The ratio a between the predicted saturation value tpTRM_∞^* and the initial tail tpTRM_1^* for all natural samples is about 1.6 with astonishingly little variation. Both synthetic samples, however, show markedly higher ratios close to 2; also their ratios between tpTRM_1^* and pTRM_1^* are much higher than for the natural samples.

Table 1. Least square fit parameters a, b, λ for approximating the experimental data by (11).

Sample	$\mathrm{tpTRM}_1^*/\mathrm{pTRM}_1^*$	a	b	λ
B	11.8 per cent	2.004	1.451	0.659
1109	8.6 per cent	1.574	0.825	0.658
7b	7.6 per cent	1.545	0.652	0.790
11b	4.3 per cent	1.593	0.744	0.773
JM-1	14.1 per cent	1.866	1.018	0.812
12b	7.9 per cent	1.635	0.606	0.804

In contrast to tpTRM_k^*, the sequence of the measured pTRM_k^* values does not behave uniformly for the six samples in Fig. 3. It can either decay as in samples B and 1109, it can remain nearly constant as for samples 7b and 12b and it can increase as in samples 11b and JM-1. In almost all cases the numerical sum $\mathrm{pTRM}_k^* + \mathrm{tpTRM}_k^*$ increases. Only in sample B does it remain constant over all iterations.

The above experimental results correspond well with the predictions of Section 2. All tested MD samples show an increase of tpTRM_k^* with steepest slope at the beginning, even if pTRM_k^* decreases. The observed asymptotic saturation can be physically interpreted in terms of domain state stabilization, either due to a statistical process as proposed here or as a result of irreversible changes in the defect structure of the sample. The latter could be effected by a fixation of domain walls by defects which at elevated temperature move towards energetically favourable positions (diffusive after-effect). In this case the possible iterative remanence gain $\mathrm{tpTRM}_\infty^*/\mathrm{tpTRM}_1^*$ should be higher for defect-rich materials. This contrasts with the result that highest gain is observed for hydrothermally produced synthetic material (JM-1) which is defect poor.

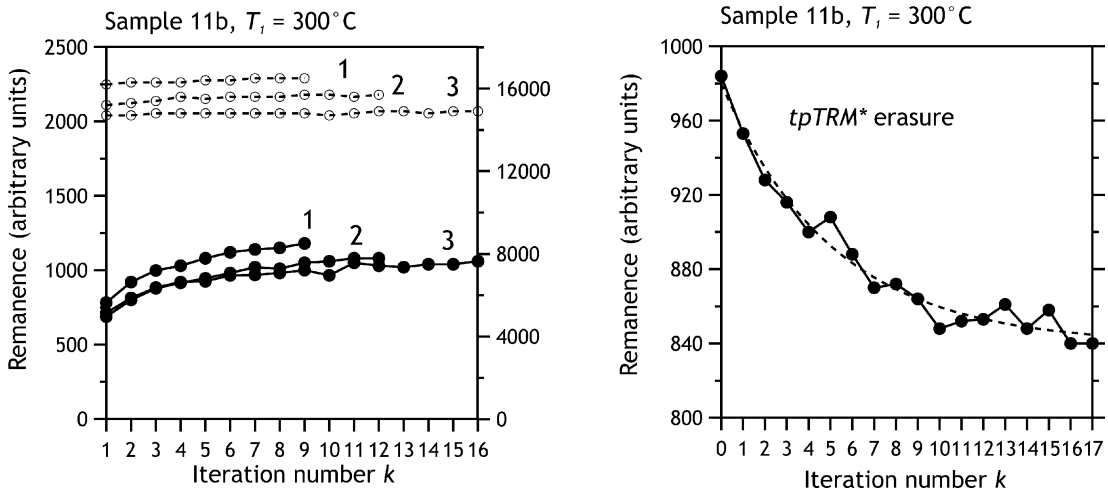

Figure 4. Left: Three repetitive experiments on sample 11b show that within 10 per cent error the experiment is repeatable. Irreversible changes during previous thermal treatment should yield deviations in the opposite direction from that observed. Deviations between the experiments are therefore attributed to drift in the experimental set-up. Right: Iteration of a tpTRM* deletion process shows exponential decay as predicted from theory. The dashed line is the best exponential fit (see text).

To further test whether irreversible change of the sample is responsible for the observed increase of tpTRM_k^* the acquisition experiment for sample 11b has been repeated three times after heating to T_C. As shown in Fig. 4 the experiment is repeatable within its error bounds. Absolute values of tpTRM_k^* for the second and third run are a bit smaller than in the first run. This is probably due to instrumental or temperature drift since the relative values normalized to the initial value at $k = 1$ coincide perfectly. In the case of irreversible changes of the defect structure one would expect to observe increasing values of tpTRM_1^* for subsequent runs. Therefore, repetition of the experiment provides no evidence for the presence of an irreversible diffusive after-effect as the primary source of the observed domain state stabilization. The statistical interpretation proposed here claims that only the probability distribution over the domain states is stabilized by iterative processes—not the domain states themselves. Irreversible changes of the defect structure are not required to explain domain state stabilization.

A further experiment investigated the decay behaviour of the iteratively acquired tpTRM_n^*, when subsequently erased by an also iterative zero field heating and cooling process with upper temperature T_1 (see Fig. 5).

A similar argument as for tpTRM* predicts exponential decay of the residual remanence to some equilibrium value, since the kth iteration of the erasure process P_{erase} with corresponding transition matrix $\mathbf{M}(P_{\mathrm{erase}})$ produces the density distribution

$$\left|\rho_{\mathrm{erase}}^{(k)}\right\rangle = \mathbf{M}(P_{\mathrm{erase}})^k \left|\rho_{\mathrm{erase}}^{(0)}\right\rangle. \tag{12}$$

The experimentally obtained remanence $m_{\mathrm{d}}^{(k)} = \langle m|\rho_{\mathrm{erase}}^{(k)}\rangle$ after the kth erasure step can be fit by the exponential decay law

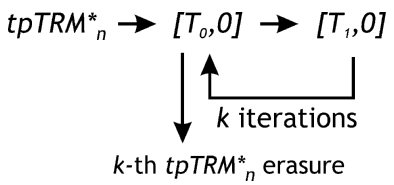

Figure 5. Process of iterative erasure of a previously acquired tpTRM_n^*.

$$m_{\mathrm{d}}^{(k)} \big/ m_{\mathrm{d}}^{(0)} = a + b\lambda_{\mathrm{d}}^k, \tag{13}$$

where $a = 0.853$, $b = 0.143$ and $\lambda_{\mathrm{d}} = 0.823$ are obtained from a least-squares fit of the data in Fig. 4(b). It is remarkable that the remaining remanence in the limit $k \to \infty$ still is larger than the initial tpTRM_1^*.

5 DISCUSSION

5.1 Outline of a quantitative interpretation

The experiments of the previous section show that the the qualitative behaviour of the iterative the tpTRM* process is correctly predicted by the statistical theory. It is now of interest whether the measurements can help to identify some of the central quantities of the abstract theory. According to eq. (5) the remanence as a function of iteration number k is related to the eigenvalues or the *spectrum* of the transition matrix $\mathbf{M}$ of the iterative process. The constant term m^∞ is due to an eigenstate to the principal eigenvalue 1. The variation with k is related to the *subdominant* eigenvalues $\lambda_{(j)}$ with $|\lambda_{(j)}| < 1$ which together form the *subspectrum* of $\mathbf{M}$.

In the experiments it has been observed that the remanence saturation curve for $k \geq 1$ is easily fitted by a single exponential function, whilst the initial step from $k = 0$ to $k = 1$ cannot be satisfactorily represented by this function. Here, a number of numerical investigations are presented to study which structural properties of the transition matrix can account for this phenomenon. The simplest explanation suggests that the subspectrum is bimodal with one mode close to 0 and the other close to the optimal fit value of λ. A physical interpretation relates these two modes to remanences with unblocking temperatures below or above T_1, respectively.

5.2 Numerical experiments on random stochastic matrices

Numerical and heuristic evidence collected in the appendix demonstrates that for a random stochastic $n \times n$ matrix with equidistributed entries the complex subspectrum is almost certainly contained in a circle with centre at 0 and radius $r_n \approx 3.7/\sqrt{n}$. For large n—as occurs in an MD ensemble state space—this would enforce immediate

relaxation into the principal eigenstate. Therefore, the equilibrium state m^∞ of the process described by such a matrix is almost immediately reached:

$$\mathrm{tpTRM}^*_1 = \mathrm{tpTRM}^*_k, \quad \text{for } k \geq 1. \tag{14}$$

This is in conflict with the presented observations for the tpTRM* process and indicates that the transition matrix $\mathbf{M}$ of this process is not modelled correctly by an equidistributed random stochastic matrix.

One possibility to explain slower approximation is to assume that at every iteration only few states actually change in course of the tpTRM* process. Then, for most states S_i the transition $S_i \rightarrow S_i$ is most probable and M_{ii} is systematically larger than the other matrix coefficients. If only with probability ϵ a state can randomly change into another, this corresponds to the mathematical assumption that the structure of the transition matrix $\mathbf{M}$ is better modelled by a random matrix of the form

$$\mathbf{M} = (1-\epsilon)\mathbf{I} + \epsilon\mathbf{A}, \tag{15}$$

where $\mathbf{A}$ is a random stochastic matrix with equidistributed random coefficients and $\mathbf{I}$ denotes the identity matrix. For a subdominant eigenvalue λ of $\mathbf{M}$ one obtains that

$$\frac{\lambda - (1-\epsilon)}{\epsilon} \tag{16}$$

is an subdominant eigenvalue of $\mathbf{A}$ and according to the numerical results almost certainly

$$|\lambda - (1-\epsilon)| < 3.7\frac{\epsilon}{\sqrt{n}}. \tag{17}$$

If n is sufficiently large, λ is therefore very well approximated by $1-\epsilon$. This, however, implies that the approach to equilibrium behaviour for the magnetization, to a good approximation, would follow the equation $m^{(k)} \approx m^\infty[1-(1-\epsilon)^k]$. Adjusting the two parameters m^∞ and ϵ to the measurement data of the previous section results in relatively poor fits. As noted before, the reason is that starting from $\mathrm{tpTRM}^*_0 = 0$, the initial increase to tpTRM^*_1 is too high compared with the subsequent increase to tpTRM^*_2 and so on.

5.3 A physical model of the transition matrix

The latter observation leads to another physically motivated model schematically illustrated in Fig. 6. Here each state S_i is considered in the transition matrix $\mathbf{M}$ as a product of the single-particle domain states. If these domain states are relatively independent, i.e. magnetostatic particle interaction is less important, it is possible to transform $\mathbf{M}$ into an approximate block matrix by synchronously reordering rows and columns. The nearly uncoupled blocks of the reordered matrix constitute more or less independent stochastic matrices. Especially, the independent blocks B_k can have different values of ϵ_k in the mixture $B_k = (1-\epsilon_k)\mathbf{I} + \epsilon_k\mathbf{A}_k$ with a random stochastic matrix $\mathbf{A}_k$. Physically, high values of ϵ_k represent MD particle populations which are more easily changed during the tpTRM* process and low values of ϵ_k represent MD particles which are not affected at all or only with a small probability. In principle, this model allows for an arbitrary distribution $d(\lambda)$ of eigenvalues over the interval [0, 1]. It is not possible to infer much detail about $d(\lambda)$ beyond the fact that it appears to be bimodal. The exponential fit used for data description in eq. (11) corresponds to a discrete spectrum with two components at the subdominant eigenvalues 0 and λ. However, numerical experiments show that bimodal continuous polynomial spectra with the same number ($N = 3$) of adjustable

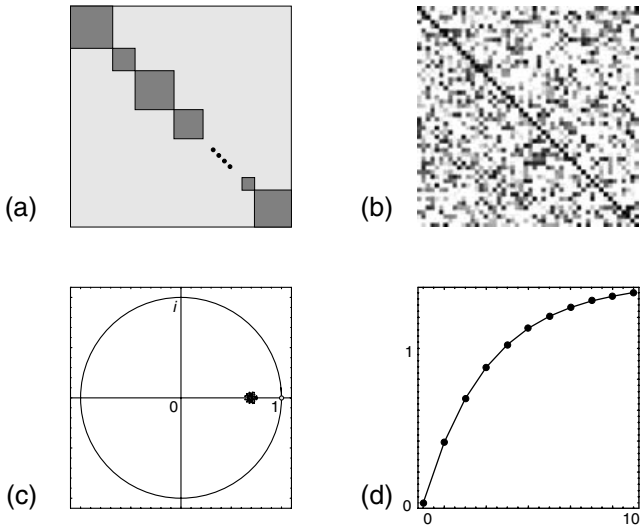

Figure 6. Speculative structure of the transition matrix $\mathbf{M}$. After synchronously reordering rows and columns a near block structure can be obtained (a). Each block (dark shaded) is a near stochastic submatrix which corresponds to a single MD particle interacting only weakly with the rest of the sample. Accordingly, light shaded areas contain entries $\ll 1/N$, where $N \times N$ is the matrix size. Each dark shaded block in (a) is a convex mixture of a random stochastic matrix $\mathbf{A}$ and the identity matrix $\mathbf{I}$. In (b) such a block B of size 50×50 is shown. $B = (1-\epsilon)\,\mathbf{I} + \epsilon\,\mathbf{A}$, where $\epsilon = 0.3$. The grey scale ranges from white (0) to black (1). The spectrum of B is depicted in (c). The principal (Frobenius) eigenvalue 1 is separated from the subspectrum of eigenvalues which cluster tightly around $\overline{\lambda} = 0.70 \approx 1-\epsilon$. The radius of the subspectrum in this case is $\rho_2 \approx 0.06$. In (d) a remanence acquisition curve modelled by iterating B is shown. A random point antisymmetric vector $\langle m|$ and a random point symmetric initial state.

parameters as the above discrete fit can explain the observations at least equally as well. In contrast, all tested three-parameter fits using *unimodal* continuous spectra deviate considerably from the measured data.

This result indicates that two different physical mechanisms for tpTRM* acquisition exist. The first mechanism is related to blocks of $\mathbf{M}$ with subdominant eigenvalues close to 0. It probably represents MD particles with many possible domain structures separated by low energy barriers which can be easily overcome below T_1. These particles change their domain structure during each iteration of the tpTRM* acquisition process, but on average do not change their average remanence acquired at the first iteration. They are responsible for the immediate step-like increase from zero remanence to tpTRM^*_1. In the classical interpretation the first mechanism corresponds to remanences with blocking temperature below T_1. The second mechanism is related to blocks of $\mathbf{M}$ with subdominant eigenvalues close to λ. It represents particles the domain structure of which most probably remains unchanged during the tpTRM* acquisition process and classically are considered as 'blocked'. Yet, during iteration they still have the capacity to stepwise adjust their domain structure. This statistical adjustment leads to a gradual stabilization. Again two possible processes are conceivable for its explanation. Either the domain state adjustment occurs by directly overcoming energy barriers which at T_1 are still relatively low and therefore will 'unblock' at temperatures only slightly above T_1. In this case domain state stabilization at T_1 is closely related to blocking and unblocking at temperatures slightly above T_1 as recently suggested by Leonhardt & Krása (2004) based on fits to experimental data.

On the other hand, domain state stabilization could be effected indirectly by regular domain changes with unblocking temperatures below T_1 which occur in the same grain and via domain reorganization increase energy barriers for remanences already blocked in other regions of the particle.

All the above different mechanisms do not exclude each other and do not even necessarily occur in separate grains. It also is imaginable that different regions of the same particle show different behaviour with respect to these mechanisms.

5.4 The decay experiment

The decay pattern of the erasure process in Fig. 4 is truly exponential. No initial step occurs and correspondingly the transition matrix will have a unimodal subspectrum with a peak at the decay exponent λ_d. Remanences with unblocking temperature below T_1 are already demagnetized after the previous tpTRM* acquisition step and cannot generate a rapid remanence loss at the first demagnetization step. Therefore, only remanences which previously have been iteratively stabilized are demagnetized now. If they behave exactly as during acquisition, the relation $\lambda = \lambda_d^2$ should hold. For sample 11b, Table 1 gives $\lambda = 0.773$, while fitting of Fig. 4 yields $\lambda_d^2 = 0.678$. Thus, remanence decay is more rapid than acquisition.

5.5 Significance for MD TRM theories

The Thellier experiment of palaeointensity determination and its modifications rely on repetitive heating and cooling of the sample (Thellier & Thellier 1959). Since remanence carriers in most rocks are not ideal single-domain (SD) particles, the response of MD remanence during this experiment is of central importance. The optimal way of performing palaeointensity determinations is not known. For example, the question of whether heating steps prior to pTRM acquisition should be performed within or without an external field has not been solved (Levi 1975; Calvo *et al.* 2002; Biggin & Böhnel 2003). A satisfactory treatment of such problems should be based on a physical theory, although a final presentation in terms of a phenomenological model might be conceptually simpler (Leonhardt & Krása 2004).

The results from our iterated tpTRM* experiments coincide very well with their statistical description (Fabian 2003). In contrast, previous theories of MD TRM cannot account for the observed effects. Thus the presented results can serve as an experimentally and theoretically confirmed benchmark for improved physical or phenomenological models of MD TRM. The full statistical theory in its present state cannot be directly used for the interpretation of palaeointensity experiments. Yet, its application to this problem is the topic of current research.

6 CONCLUSIONS

(1) Exponential remanence behaviour of MD samples during iterative thermal processes is correctly predicted by a non-equilibrium statistical theory of thermoremanence.

(2) Domain state stabilization during iterative thermal treatment is not due to the fixation of *individual* domain structures. Instead, iteration gradually brings the statistical domain state distribution into an eigenstate of the transition matrix of the process. What stabilizes is *probability density*, not domain structure.

(3) Accordingly, irreversible changes by chemical alteration, stress release or defect movement are not central to the explanation of iterative domain state stabilization.

(4) The transition matrix of tpTRM* acquisition in MD samples has a bimodal subspectrum. The first mode describes an immediate tail generation probably in particles with low energy barriers. The second mode is related to a creeping stabilization, probably related to higher energy barriers or remanence acquisition at higher blocking temperatures.

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APPENDIX A: SPECTRAL PROPERTIES OF STOCHASTIC MATRICES

Transition matrices $\mathbf{M}$, as considered in the statistical theory of MD TRM, are *stochastic matrices*. Their entries denote transition probabilities between a complete set of possible states S_i. This implies that all entries are non-negative and that the sum over each column of the matrix $\mathbf{M}$ is 1. For such matrices, the set of eigenvalues (spectrum) has very special properties as stated by the theorem of Frobenius and Perron.

$M_{ij} := P(S_j \rightarrow S_i)$

Frobenius–Perron theorem

For all eigenvalues λ_k of a transition matrix $\mathbf{M}$ is $|\lambda_k| \leq 1$. $\lambda_1 = 1$ is an eigenvalue of $\mathbf{M}$ which has a non-negative eigenvector $\mathbf{v} \geq 0$.

Proof: For any vector $\mathbf{v}$ we have for the sum of the components of $\mathbf{Mv}$

$$\left| \sum_{i,j=1}^{N} M_{ij} v_i \right| = \left| \sum_{i=1}^{N} v_i \right| .$$

Thus for any eigenvector $\mathbf{v}$ with $\mathbf{M}\,\mathbf{v} = \lambda\mathbf{v}$ we have $\lambda \sum_i v_i = \sum_i v_i$ which can be fulfilled either when $\lambda = 1$ or when $\sum_i v_i = 0$. Since all vectors fulfilling the latter condition only span a vector space with dimension $N - 1$ there must exist at least one eigenvector with eigenvalue 1. Since $\|\mathbf{Mv}\|_1 \leq \|\mathbf{v}\|_1$ all eigenvalues are ≤ 1. $\mathbf{M}$ therefore is a contraction which maps the compact set of non-negative unit vectors into itself. Thus, according to Schauder's fixed point theorem, $\mathbf{M}$ possesses a non-negative fixed point $\mathbf{v}$ which is a non-negative unit eigenvector to the eigenvalue 1. (Frobenius and Perron).

The above properties imply that by repetition of an iterative process the system will approach an eigenstate to the eigenvalue 1. All other contributions to the initial ρ_0 decay exponentially with the number of iterations. Since $\sum_i \rho_i = 1$ the vector ρ has a non-zero component in the eigenspace of $\lambda = 1$. Otherwise $\sum_i \rho_i$ would be zero as shown above. If some states (particles) are not influenced by an iterative process P, the eigenspace of $\lambda = 1$ of $\mathbf{M}(P)$ is degenerate.

The set of all eigenvalues of all n-dimensional stochastic matrices is exactly described by a theorem of Karpelevič (Karpelevič 1951; Ito 1997). In the limit $n \rightarrow \infty$ it asymptotically fills the whole unit disc.

Subdominant eigenvalues λ with $|\lambda| = 1$ occur only for permutation cycles, which in the case of transition matrices correspond to cyclic transitions $S_{i_1} \rightarrow S_{i_2} \rightarrow \cdots \rightarrow S_{i_k}$. The eigenvalues of permutation matrices consisting of only one cycle of length k are exactly the kth roots of unity. Consequently, large subdominant eigenvalues correspond to highly probable permutation cycles of states or—equivalently—to near uncoupling of state subspaces (Hartfiel & Meyer 1998).

The subspectrum of iterated stochastic matrices

Although non-negative matrices, due to their relevance in the theory of Markov processes, have been studied for a long time, astonishingly little is known about the general structure of their subspectrum.

Here a numerical approach is used to investigate the subspectrum of random stochastic matrices with equidistributed entries. A random stochastic $n \times n$ matrix $\mathbf{M}$ is constructed by first choosing n^2 independent equidistributed random numbers $a_{ij} \in [0, 1]$. The final matrix coefficients M_{ij} are calculated by normalizing the columns according to

$$M_{ij} = \frac{a_{ij}}{\sum_{k=1\ldots n} a_{ik}}. \tag{A1}$$

Then all complex eigenvalues of $\mathbf{M}$ are calculated.

The results of many thousands of such experiments are shown in Fig. A1. They indicate that the average subspectral radius $\rho_{2,n}$ of an equidistributed random $n \times n$ stochastic matrix decreases as $2.6\, n^{-1/2}$ and for sufficiently large n almost certainly all eigenvalues lie in a disc of radius $3.7n^{-1/2}$ centred at the origin.

A note on the heuristic interpretation

Assume that $\mathbf{A}$ is a random $n \times n$ stochastic matrix and λ is an element of its subspectrum. Using the central limit theorem on the construction in (A1), one can show that for equidistributed $\mathbf{A}$, each entry a_{ji} is asymptotically equidistributed on the interval $[0, \frac{2}{n}]$. For each subdominant eigenvalue λ, there exists an eigenvector $\mathbf{x}$ such that for x_m with $|x_m| = \max |x_i|$ we have

$$|\lambda| = \lambda x_m = \sum_{j=1}^{n} a_{ji} x_i = \sum_{i=1}^{n} a_{mi} \mathrm{Re}(x_i). \tag{A2}$$

The equidistributed coefficients $a_{mi} \geq 0$ are not independent since their sum is 1. Similarly, the numbers $\mathrm{Re}(x_i) \in [-1, 1]$ are not independent since their sum is zero. Moreover, a_{mi} and $\mathrm{Re}(x_i)$ depend on each other since the eigenvector $\mathbf{x}$ can be expressed in terms of the coefficients of $\mathbf{A}$. Yet it is plausible that these dependences are rather weak and consequently these numbers in the statistical sense are nearly independent. Under this (unproven) hypothesis, the right hand side of (A2) can be interpreted as an undirected n-step 1-D random walk with average step size $d \propto \langle a_{ji} |\mathrm{Re}(x_i)| \rangle \propto \frac{1}{n}$. Thus, the average distance of the endpoint from the origin is proportional to $d\sqrt{n} \propto \frac{1}{\sqrt{n}}$. The average maximal distance obtained during $n - 1$ independent similar walks (for each eigenvalue of A) also is proportional to $\frac{1}{\sqrt{n}}$. According to this heuristic argument, the subspectrum of large $n \times n$ random stochastic matrices will contract in proportion to $\frac{1}{\sqrt{n}}$ as numerically observed in Fig. A1. However, a strict proof that the subspectral radius converges to zero exists only in the special case of doubly stochastic matrices (Berkolaiko 2001). It crucially relies on the fact that for a doubly stochastic matrix $\mathbf{M}$ the matrix $\mathbf{M}^{\mathrm{T}}\mathbf{M}$ is again stochastic. Therefore, this proof cannot be easily modified to yield the same result for general stochastic matrices.

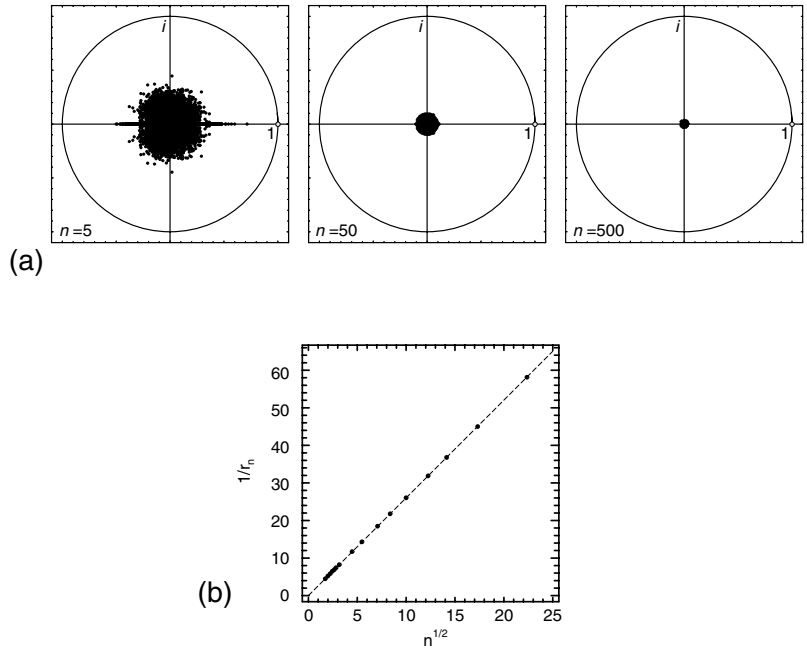

Figure A1. Subspectra of random stochastic matrices. Each plot in (a) shows the union of at least 10 000 eigenvalues of randomly generated stochastic $n \times n$ matrices. Apparently, this union is contained almost certainly within a circle of radius ρ_n, which decreases like $1/\sqrt{n}$. In (b) the inverse of the average distance r_n of the eigenvalues from the origin is plotted as a function of $\sqrt{n}$, yielding a straight line with slope $\approx$2.6.