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Statistical theory of weak field thermoremanent magnetization in multidomain particle ensembles

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SUMMARY

A non-equilibrium statistical theory of multidomain thermoremanent magnetization (TRM) is developed, which describes thermal magnetization changes as continuous inhomogeneous Markov processes. The proposed theory relies on three very general physical properties of TRM: (a) The probability that a magnetization state S_j is transformed during an infinitesimal temperature change into state S_i depends only on external conditions and on S_j, but not on previously assumed states. (b) Due to time inversion symmetry of the Maxwell equations, the magnetic energies are invariant with respect to inversion of all spins in zero field. (c) The probability that an energy barrier between two magnetization states is overcome during a thermal process is governed by Boltzmann statistics. From these properties, the linearity of TRM with field is derived for generic multidomain particle ensembles. The general validity of Thellier's law of additivity of partial TRM's in weak fields is established and a method for proving a large class of similar additivity laws is developed. The theory allows consistent treatment of blocking and unblocking of remanence in multidomain particle ensembles and naturally explains apparent differences between blocking and unblocking temperatures.

Key words: remanent magnetization, rock magnetism, thermomagnetic analysis, transdomain changes.

1 INTRODUCTION

The thermoremanent magnetization (TRM) of natural rocks is the most important geophysical archive for information about direction and intensity of the Earth's magnetic field in former times. Thermoremanence data are used to reconstruct the details of plate tectonics as well as the history of the geodynamo. Especially for the measurement of palaeointensities of the Earth's magnetic field it is a major problem that a reliable theory of TRM exists only for single-domain (SD) particle ensembles (Néel 1949). The magnetic fraction in natural rocks, however, consists mainly of multidomain (MD) or so called pseudo-single domain (PSD) particles, which—with respect to the problems treated here—can be regarded as small MD particles.

Physical theories of MD TRM so far mainly focus on very special cases like that of rectangular particles with one domain wall (Néel 1955; Schmidt 1973). In order to deal with more realistic applications, a number of theories have been proposed, which either radically extrapolate results from the above two domain model (Shcherbakov 1981; Dunlop & Xu 1994; Xu & Dunlop 1994) or are based on analogies between MD TRM and physical phenomena like quasi single domain moments (Verhoogen 1959; Halgedahl 1991) or spin glasses (Shcherbakov *et al.* 1993; Ye & Merrill 1995).

Experimental results indicate that TRM acquisition is essentially a stochastic process which requires statistical physics for its description. Repeated microscopic observations of the same TRM acquisition process leave the particle in different domain structures at room temperature (Halgedahl 1991). Observations of magnetization states of natural large MD magnetite at different temperatures proved that domain wall position and average domain width vary considerably with temperature (Heider *et al.* 1988; Heider 1990; Ambatiello *et al.* 1999). This also indicates that, besides domain wall pinning, domain nucleation is of major importance during TRM acquisition (Moon & Merrill 1985), especially in MD particles with low internal stress (Muxworthy 2000). These and similar experiments, as well as micromagnetic calculations for small PSD particles (Enkin & Dunlop 1987; Enkin & Williams 1994; Winklhofer *et al.* 1997) lead to the conclusion that the magnetic energy landscape of MD particles contains many local minima with statistically distributed energy barriers between them. Therefore, one has to take into account that transitions between domain states are induced not only by systematic influences but also by random thermal fluctuations. As a consequence, the correct theoretical description of thermal magnetization processes should be based on concepts of non-equilibrium statistical physics.

In order to understand the systematic trends behind the results of the last decade of experimental investigation, purely mathematical or phenomenological models have recently been developed. They describe coherently the outcome of many experimental facts of MD TRM (Shcherbakova *et al.* 2000; Fabian 2000). These models can be used for first order modelling of measurement procedures, but their physical background is not understood. Therefore it is difficult to

estimate the conditions for their validity. The purpose of this article is to establish a physical theory of MD TRM which consistently explains the experimental observations by means of non-equilibrium statistics.

The central concept in the following line of reasoning is to replace the actual change in domain state during a thermal process by a probability density over all possible domain changes. This allows to keep track of two antisymmetric paths of domain change at the same time. In zero field, antisymmetric paths have the same probability but produce opposite remanences. This, by the way, explains why on average the remanence after zero field cooling is zero. Going through the mathematical difficulties of linearly expanding the transition probabilities with respect to the external field is rewarded with a proof of the linearity and additivity of weak field pTRMs. But also the interpretation of blocking and unblocking of remanence is different in the statistical theory. It will be shown that the statistical interpretation naturally explains the phenomena related to blocking and unblocking processes which are very hard to interpret using deterministic MD TRM theories.

2 STATISTICAL DESCRIPTION OF THERMAL MAGNETIZATION PROCESSES

The following two subsections introduce the formal framework of the statistical description and the main physical concepts. First a thermal process is defined as a sequence of changes in either temperature or field, but not in both simultaneously. The second subsection gathers the fundamental facts about magnetization structures which will be used later.

2.1 Definition of equitemporal thermal magnetization processes

Any thermal magnetization process essentially is a thermo-viscous process since the outcome depends, sometimes critically, upon cooling or heating rates and also on residence times at temperatures and fields.

It is possible to take into account all these time dependent effects in the proposed statistical theory. However, this leads to unnecessary inconvenient formal efforts for the intended purpose. Therefore, the presentation of the theory in the following is limited to *equitemporal* thermal magnetization processes with characteristic time τ_c. This means, that heating and cooling rates of all temperature changes are equal to T_C/τ_c, where T_C denotes the Curie temperature. Moreover, all residence times are in the order of τ_c.

A T-H-process is defined as an equitemporal thermal magnetization process which is composed of one or more steps, each of which either changes field H or temperature T.

(1) A position $Z = [T, H]$ of a T-H-process is uniquely defined by its temperature T and field H.

(2) The T-H-initial or paramagnetic position is $Z_C = [T_C, 0]$. At this position samples have no ferromagnetic order and their magnetic memories are completely erased.

(3) A transition $Z_i \to Z_j$ between position $Z_i = [T_i, H_i]$ and $Z_j = [T_j, H_j]$ is admissible only if either $T_i = T_j$ or $H_i = H_j$. Synchronous changes of temperature and field are explicitly excluded.

(4) A T-H-process $P = Z_1 \to \cdots \to Z_n$ is a sequence of admissible transitions.

2.2 Fundamental facts about changes of magnetization structure during T-H-processes

A magnetic sample consists of a collection of magnetic particles each of which has its own remanence states determined by its mineralogy, size, shape, surface properties, dislocation structure, inclusions, defects, twin boundaries and other properties. In order to ensure repeatability of thermomagnetic experiments, the samples in the following are assumed to be thermally stable. This means that repeated measurements of thermal magnetization processes starting from the paramagnetic position lead to the same results. Therefore, neither chemical changes nor long-term diffusive after-effects must occur at elevated temperatures. Despite the variety of remaining possible influences, the following physical assertions can be made about the magnetic structure of the MD sample.

(1) The magnetic particle ensemble can assume different positive irreversible states S_i, $i \in \{1, \ldots, N\}$. For each state S_i there exists an antisymmetric state $S_{-i} = -S_i$ obtained by inversion of the magnetic spin structure. The state $S_0 = -S_0$ denotes the disordered paramagnetic state above T_C.

(2) To each irreversible state S belongs a reversible region Rev(S) of states, which can be reversibly reached from S by changes in field and temperature. Typical examples for reversible processes are domain wall bowing, shift of unpinned walls or reversible rotation of magnetization spins. Two states within the same reversible region can be transformed into each other without energy dissipation, while transformations between two different irreversible states always dissipate energy.

(3) To each irreversible state S and each temperature T a magnetization $m(S, T)$ is assigned. For states S which can exist in zero field at temperature T, $m(S, T)$ is defined such, that $M_S(T)\, m(S, T)$ denotes the remanence of the sample in the zero field state of Rev(S) at temperature T. Here, $M_S(T)$ refers to the saturation magnetization. It follows that $m(-S, T) = -m(S, T)$.

(4) The state of a sample after some T-H-process can be characterized by a probability density vector $\rho_i \geq 0$ which denotes the probability that the irreversible state of the sample after this process is S_i. Since the sample is always in one of the possible states, $\sum_{i=-N}^{N} \rho_i = 1$. Note that ρ_i is a vector only in the mathematical, not in the physical sense.

Fig. 1 sketches an example for a small number of domain states within an MD particle. These domain states are the irreversible states of this particle. While for a single particle it is an easy and correct way to visualize the theoretical notion of 'irreversible state'

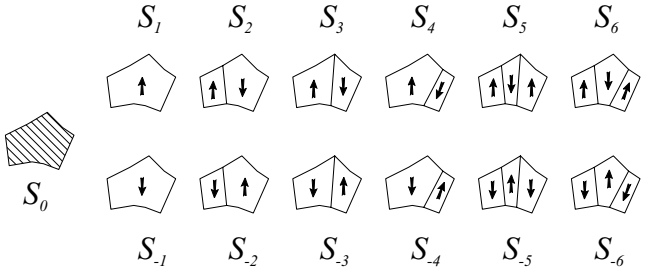

Figure 1. An example of a simple system of different irreversible magnetization states within a single MD particle. State S_0 is the paramagnetic state without ferromagnetic order. States $S_{-1}, \ldots, S_{-6}$ are inverse to states $S_1, \ldots, S_6$. The abstract notion of 'state' used in the text includes simple systems like this, but also interacting ensembles of many magnetic particles with different mineralogy.

as 'domain state', one has to keep in mind that in general 'irreversible state' refers to a huge collection of domain configurations in many MD particles simultaneously and N will be astronomically large. In the remaining article, a statement like 'the sample is in state S_i' means that it is in one of the states of Rev (S_i) belonging to the irreversible state S_i. Especially, if the irreversible state doesn't change during a T-H-process, reversible changes may still occur.

2.3 Statistical description, transition matrix

During heating or cooling the material properties of the particles vary. This considerably changes the topography of the magnetic energy landscape. Changes in magnetization structure occur as soon as formerly too high energy barriers are overcome by thermal energy during the temperature change. As thermal activation is involved here, such transitions are essentially of a statistical nature. Typical examples of sudden transitions between local energy minima are unpinning of domain walls and nucleation or denucleation of magnetic domains. If more than one energy barrier becomes sufficiently low at some temperature, it is impossible to predict which of the several possible magnetization changes actually takes place. Yet, using statistical physics it is possible to calculate the probability of each transition and to infer the change in the probability distribution over the irreversible states. If this probability distribution is known in the initial T-H-position, the change in magnetization state induced by some T-H-process can be described by means of a transition matrix.

For two adjacent T-H-positions $Z = [T, H]$ and $Z' = [T', H']$ the nonnegative transition matrix $M_{ij}(Z \to Z') \geq 0$ denotes the probability that the irreversible state S_j is transformed to state S_i by the process $Z \to Z'$. It follows that $\sum_i M_{ij} = 1$ for all j since after the process the system must be in one unique state. Such a matrix often is denoted as a stochastic matrix (Seneta 1973). The probability density vector $\rho(Z)$ with $\sum_i \rho_i(Z) = 1$ is changed by the transition according to

$$\rho(Z') = M(Z \to Z')\rho(Z). \tag{1}$$

Stochasticity of M ensures that again $\sum_i \rho_i(Z') = \sum_{i,j} M_{ij}\rho_j(Z) = 1$. State transitions are Markov processes because the probability density after the transition depends only on the initial probability density of irreversible states and not on the previous history which describes how the initial probability density was reached. For a T-H-process $P = Z_1 \to \cdots \to Z_n$ consisting of several steps, the transition matrix $M(P)$ is the matrix product

$$M(P) = M(Z_{n-1} \to Z_n)M(Z_{n-2} \to Z_{n-1}) \ldots M(Z_1 \to Z_2). \tag{2}$$

Application of (1) to the change of density induced by a small increase of temperature $[T, H] \to [T + \Delta T, H]$ yields

$$\begin{aligned}\rho([T + \Delta T, H]) - \rho([T, H]) \\ = (M([T, H] \to [T + \Delta T, H]) - \mathrm{Id})\,\rho([T, H]),\end{aligned} \tag{3}$$

where Id denotes the identity matrix. Division by ΔT and taking the limit $\Delta T \to 0$ results in the linear differential equation

$$\frac{\partial \rho}{\partial T}([T, H]) = \mu(T, H)\rho([T, H]), \tag{4}$$

where

$$\mu(T, H) := \lim_{\Delta T \to 0} \frac{M([T, H] \to [T + \Delta T, H]) - \mathrm{Id}}{\Delta T}, \tag{5}$$

is the *infinitesimal generator* of the Markov process. Sometimes (4) is called the *master equation* of the non-equilibrium thermodynamic system. In the same way, a small field step $[T, H] \to [T, H + \Delta H]$ leads to a master equation for field changes

$$\frac{\partial \rho}{\partial H}([T, H]) = \nu(T, H)\rho([T, H]), \tag{6}$$

with infinitesimal generator

$$\nu(T, H) := \lim_{\Delta H \to 0} \frac{M([T, H] \to [T, H + \Delta H]) - \mathrm{Id}}{\Delta H}. \tag{7}$$

It must be stressed, that these infinitesimal generators depend on cooling rate and residence times which for the sake of simplicity in the present formulation are assumed to be constant.

3 TRANSITION MATRIX IN WEAK FIELDS

The master equation for temperature change (4) cannot be directly solved using matrix exponential functions, which are the standard tool for homogeneous Markov processes in non-equilibrium thermodynamics where the variable is time instead of temperature.

In case of homogeneous Markov processes the transition probabilities depend only upon temperature difference, which would require the validity of

$$M([T, H] \to [T + \Delta T, H]) = M([0, H] \to [\Delta T, H]). \tag{8}$$

This obviously is not true for MD ensembles where energy barriers and accordingly the transition probabilities depend crucially upon the absolute value of T. This case is therefore regarded as an inhomogeneous Markov process.

The mathematical tools necessary to deal with inhomogeneous Markov processes are given in Appendix A. In this section the transition matrix for a temperature change in a weak external field is related to the zero-field transition matrix for the same temperature change. Special attention is focused on the symmetry properties of transitions between inverse states which are of crucial importance for the subsequent line of reasoning.

Definition: A matrix $M \in \mathbb{R}^{(2n+1)\times(2n+1)}$ is point symmetric if, and only if, $M_{ij} = M_{-i-j}$ for all indices $i, j = -n, -n + 1, \ldots, n - 1, n$. M is point antisymmetric if, and only if, $M_{ij} = -M_{-i-j}$ for all i, j.

One easily verifies the following properties:

(1) A linear combination of point (anti-)symmetric matrices is again point (anti-)symmetric.

(2) The product of two point (anti-)symmetric matrices is point symmetric.

(3) The product of a point symmetric and a point antisymmetric matrix in any order is point antisymmetric.

Fundamental physical time inversion symmetry implies that in zero field a transition $S_j \to S_i$ has the same probability as the transition $-S_j \to -S_i$ because inversion of the time arrow reverses all spins and external fields, but leaves transition probabilities unchanged. Consequently, zero field transition matrices are point symmetric. The main result of this section is, that the difference between an in-field transition matrix and the corresponding zero-field transition matrix can be expanded into a Taylor series, the linear part of which is point antisymmetric. This means that when a transition $S_j \to S_i$ becomes more likely within a small field, its inverse transition $-S_j \to -S_i$ becomes more unlikely by the same amount. The formal proof relies upon properties of solutions of homogeneous systems of linear differential equations depending upon a parameter h (field in this case), which are stated in the first part of Appendix A.

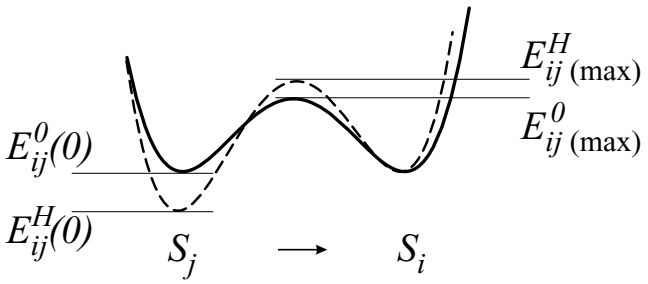

Figure 2. Change of energy barrier due to a weak external field H. Note that the change of barrier height results from both, the change of the energy in the minimum state S_j and the change of the maximum energy.

The micromagnetic energy $E(T, H, m)$ of the MD particle ensemble is a function of temperature, field and of the combined magnetization structure m of all particles. For fixed T and H it defines a real valued functional on an infinite dimensional configuration space. The local minima of $E(T, H, m)$ coincide with the irreversible states S_i. During the transition from state S_j into S_i an energy barrier has to be overcome. In the following it will be calculated how this energy barrier changes with respect to the zero-field case when a weak field H is applied.

Let $S^H_{ij}(t)$ for $t \in [0, 1]$ denote the optimal transition path between two states S_j and S_i when cooling from T to $T - \Delta T$ in an external field H. Thus $S^H_{ij}(0) = S^H_j \in \mathrm{Rev}(S_j)$ and $S^H_{ij}(1) = S^H_i \in \mathrm{Rev}(S_i)$. Along this transition path the magnetic energy in field H is denoted by $E^H_{ij}(t)$ and the magnetization by $M_s(T)m^H_{ij}(t)$. From the sketch in Fig. 2 it can be seen that the zero-field energy barrier for this transition is $\Delta E^0_{ij} = E^0_{ij(\max)} - E^0_{ij}(0)$. For the in-field transition we obtain in first order

$$E^H_{ij(\max)} = E^0_{ij(\max)} + H\mu_0 M_s(T) m^0_{ij(\max)}, \tag{9}$$

where $m^0_{ij(\max)}$ is the zero-field magnetization in the state with energy $E^0_{ij(\max)}$. Accordingly

$$\Delta E^H_{ij} = \Delta E^0_{ij} + H\mu_0 M_s(T)\left(m^0_{ij(\max)} - m^0_j\right). \tag{10}$$

For the transition between S_{-j} and S_{-i} we obtain by symmetry that $S^0_{-i-j}(t) = -S^0_{ij}(t)$ and $m^0_{-i-j}(t) = -m^0_{ij}(t)$. Therefore

$$\Delta E^H_{-i-j} = \Delta E^0_{ij} - H\mu_0 M_s(T)\left(m^0_{ij(\max)} - m^0_j\right). \tag{11}$$

According to Boltzmann statistics, a small change ΔE in energy barrier height changes the transition probability p^0 into $p^0\, e^{-\Delta E/kT}$. In the above case, each matrix coefficient of the in-field transition matrix

$$M^H := M([T, H] \to [T - \Delta T, H]) \tag{12}$$

is obtained by first multiplying the corresponding coefficient of M^0 by the appropriate exponential factor, which leads to

$$A^H_{ij} = \exp\left(q(T)H\Delta m^0_{ij}\right) M^0_{ij}, \tag{13}$$

where $\Delta m^0_{ij} = m^0_{ij(\max)} - m^0_j$ and $q(T) = \mu_0 M_s(T)/kT$. To finally obtain M^H from A^H, it must be ensured that $\sum_i M^H_{ij} = 1$. Thus, in first order in H the in-field transition matrix is

$$\begin{aligned} M^H_{ij} &= \frac{A^H_{ij}}{\sum_i A^H_{ij}} \\ &\approx M^0_{ij} - q(T)H\left(M^0_{ij}\sum_k \Delta m^0_{ik} M^0_{ik} - \Delta m^0_{ij} M^0_{ij}\right). \end{aligned} \tag{14}$$

In the limit $\Delta T \to 0$, the first order form of the infinitesimal generator $\mu(T, H)$ is obtained from the last expression as

$$\begin{aligned} \mu_{ij}(T, H) &\approx \mu_{ij}(T, 0)\left(1 + q(T)H\Delta m^0_{ij}\right) \\ &= \mu_{ij}(T, 0) + H\alpha_{ij}. \end{aligned} \tag{15}$$

Here the matrix $\alpha_{ij} = q(T)\Delta m^0_{ij}\mu_{ij}(T, 0)$ is point antisymmetric, i.e. $\alpha_{ij} = -\alpha_{-i-j}$. Of course, the same infinitesimal generator is obtained when the heating step $T \to T + \Delta T$ is considered.

Theorem 1 of Appendix A contains the formal solution of the master eq. (4) for the expansion of the infinitesimal generator to first order in H. From this solution it can be inferred that for a process $[T, 0] \to [T', 0]$ there is a point antisymmetric matrix $R_{ij}(T, T') = -R_{-i-j}(T, T')$ such that in first order approximation

$$M([T, H] \to [T', H]) = M([T, 0] \to [T', 0]) + HR(T, T'). \tag{16}$$

In addition to changes in temperature, the description of partial thermoremanences requires matrices $M([T, 0] \to [T, H])$ and $M([T, H] \to [T, 0])$ which switch the external field on or off. In linear approximation without viscous effects, small field changes induce only reversible magnetization changes according to Rayleigh's law. However, when residence times in the order of τ_c are considered, also weak applied fields modify the viscous transition probabilities. In the second part of Appendix A it is shown that in this case a non-zero linear term in the expansion of $M([T, 0] \to [T, H])$ may occur and that this term again is point antisymmetric.

4 THE LINEARITY OF TRM IN WEAK EXTERNAL FIELDS

Linearity of TRM(H) in sufficiently small fields is experimentally well established for SD particle ensembles, even though in strongly interacting synthetic magnetite, TRM acquisition is nonlinear above 50 μT (Dunlop & Argyle 1997). Also for most natural rocks containing PSD or MD particles TRM acquisition is linear in weak fields (Day 1977; Carlut & Kent 2002). Apparent exceptions occur for moon rocks containing large MD iron crystals (Dunn & Fuller 1972). In few rocks deviations from linearity occur in fields smaller than the Earth's magnetic field. Néel showed that thermal fluctuations explain the linear dependence in case of SD particles (Néel 1955) but MD TRM theories based on domain theoretical investigations – often called hysteretic theories – do not predict the observed linear TRM behaviour. Phenomenological MD TRM theories simply presume linearity of TRM. The first consistent phenomenological theory was built from an analogy between MD ensembles and spin glasses and derived a kinematic equation

$$\frac{d}{dT}m(T) = A(T) - B(T)\,m(T) \tag{17}$$

for the sample magnetization $m(T)$ (Shcherbakov *et al.* 1993). Only by assuming a linear dependence of $A(T)$ on H were they able to obtain linearity of TRM. The same kinematic equation has later been related to a phase theoretical model of uniaxial MD particles where it was possible to infer the linear dependence of $A(T)$ from the dependence of magnetostatic energy on external field (Fabian 2000). However, the derivation of (17) still required purely phenomenological assumptions (eq. 18 in Fabian 2000). A generally valid physical proof for the linear dependence of MD TRM on H has not yet been provided although a micromagnetic calculation including thermal fluctuations rigorously proves the linearity of TRM at the blocking temperature T_B where the MD system changes from thermal equilibrium to a non-equilibrium state (Fabian 2000). However, the occurrence of non-equilibrium transdomain processes during cooling from T_B to T_0 may well destroy this linearity—an important fact which has been pointed out in Dunlop & Xu (1994).

In this section it will be shown that the linearity of TRM(H) in weak fields for generic PSD and MD particle ensembles where

$R(T, T') \neq 0$ is an immediate consequence of the linear expansion (16).

At T_C, the sample is in state S_0, therefore the state density vector ρ_C at T_C is δ_{i0}, where δ_{ij} is the Kronecker symbol. Using the abbreviations $M^H := M([T_C, H] \rightarrow [T_0, H])$, $R := R(T_c, T_0)$ and $\rho^H = \rho([T_0, H])$ eq. (1) together with (16) becomes

$$\rho^H = M^H \rho_C = (M^0 + HR)\rho_C. \tag{18}$$

For the probabilities of the antisymmetric states S_i and S_{-i} this yields

$$\begin{aligned} \rho_i^H &= M_{i0}^0 + HR_{i0}, \\ \rho_{-i}^H &= M_{-i0}^0 + HR_{-i0} = M_{i0}^0 - HR_{i0}. \end{aligned} \tag{19}$$

The total remanence $m^H(T_0)$ at T_0 is now obtained as

$$\begin{aligned} m^H(T_0) &= \sum_{i=-N}^{N} m(S_i, T_0)\rho_i^H \\ &= \sum_{i=1}^{N} m(S_i, T_0)\left(\rho_i^H - \rho_{-i}^H\right) \\ &= 2H \sum_{i=1}^{N} m(S_i, T_0)R_{i0}. \end{aligned} \tag{20}$$

Thus $m^H(T_0)$ depends linearly on H with the exception of those extreme cases where the sum over $m(S_i, T_0)\, R_{i0}$ is zero. In these cases, a small disturbance of the entries of R suffices to restore linearity. This is what is meant by stating that all generic MD particle ensembles show linear TRM dependence.

The above result considerably extends the thermo-fluctuational theory of Néel (1955) and also the phenomenological arguments of Shcherbakov *et al.* (1993) and Fabian (2000), because non-equilibrium state transitions during the entire cooling process are consistently taken into account. However, the notion of 'weak field' in the above derivation depends upon the height of the energy barriers within the system. If these are very low, linearity may occur only at fields lower than the Earth's magnetic field. The apparent non-linearity found for interacting SD ensembles and large iron crystals (Dunlop & Argyle 1997; Dunn & Fuller 1972) thereby is not in conflict with the present calculation.

5 THELLIER'S LAW OF ADDITIVITY

One of the most astonishing experimental facts of MD TRM concerns Thellier's law of additivity. It states, that the sum of two or more pTRMs separately acquired in non-overlapping temperature intervals is equal to a single pTRM acquired in the union of these temperature intervals. Néel (1949) explained the validity of this law for ensembles of SD particles by showing that each SD particle possesses a single well defined blocking temperature. Thus pTRMs acquired in disjoint temperature intervals are carried by different particles and contribute independently to the total TRM. Several studies confirm the validity of Thellier's additivity law also for MD remanence carriers (Levi 1979; Shcherbakov *et al.* 1993; Dunlop & Özdemir 2001). When the very thorough study Levi (1979) showed that additivity of pTRM also holds perfectly for MD particles, the author at that time readily concluded that blocking within MD particles must, like in SD particles, occur at one well defined temperature which would imply that also in MD samples the pTRMs are independent. However, experiments revealed that independence of pTRMs in MD samples can be badly violated and that changes of the magnetization structure occur during the entire cooling process (Petrova & Trukhin 1961; McClelland & Sugiura 1987; Shcherbakov *et al.* 1993). Therefore, the high degree of precision with which additivity of pTRMs is fulfilled in MD samples became more and more puzzling. In the following, based on the statistical description given in the previous section, a complete physical explanation of the phenomenon of additivity is given.

To describe acquisition of pTRMs in different temperature intervals in terms of similar sequences of T-H-processes, represented by their transition matrices, the following types of matrices are needed:

$$\begin{aligned} M_{(j)}^H &:= M\left([T_{j+1}, H] \rightarrow [T_j, H]\right), \\ U_{(j)}^H &:= M\left([T_j, 0] \rightarrow [T_j, H]\right), \\ D_{(j)}^H &:= M\left([T_j, H] \rightarrow [T_j, 0]\right). \end{aligned} \tag{21}$$

The temperatures $T_C = T_5 \geq T_4 > \cdots > T_1 \geq T_0$ are the boundaries of the pTRM intervals. Fig. 3 sketches which transition matrices must be multiplied to obtain the total transition matrices $W_H^{(a)}$, $W_H^{(b)}$, $W_H^{(c)}$ for pTRM$^{(a)}$, pTRM$^{(b)}$ and pTRM$^{(c)}$. The latter is acquired over the union of the temperature intervals used for pTRM$^{(a)}$ and pTRM$^{(b)}$. Here indices (x) refer to Fig. 3.

The resulting expressions are

$$\begin{aligned} W_{(a)}^H &= M_{(0)}^0 D_{(1)}^0 M_{(1)}^0 U_{(2)}^0 M_{(2)}^0 D_{(3)}^H M_{(3)}^H U_{(4)}^H M_{(4)}^0, \\ W_{(b)}^H &= M_{(0)}^0 D_{(1)}^H M_{(1)}^H U_{(2)}^H M_{(2)}^0 D_{(3)}^0 M_{(3)}^0 U_{(4)}^0 M_{(4)}^0, \\ W_{(c)}^H &= M_{(0)}^0 D_{(1)}^H M_{(1)}^H U_{(2)}^H M_{(2)}^0 D_{(3)}^H M_{(3)}^H U_{(4)}^H M_{(4)}^0. \end{aligned} \tag{22}$$

The first order expansions $W_{(x)}^H = W_{(x)}^0 + Hw^{(x)}$ of these matrices in H can be calculated using the results of the previous sections which state that in first order

$$\begin{aligned} M_{(j)}^H &\approx M_{(j)}^0 + HR_{(j)}, \\ U_{(j)}^H &\approx U_{(j)}^0 + Hu_{(j)}, \\ D_{(j)}^H &\approx D_{(j)}^0 + Hd_{(j)}. \end{aligned} \tag{23}$$

Here the matrices $M_{(j)}^0$, $U_{(j)}^0$ and $D_{(j)}^0$ are point symmetric, while $R_{(j)}$, $u_{(j)}$ and $d_{(j)}$ are point antisymmetric. Substituting (23) into (22)

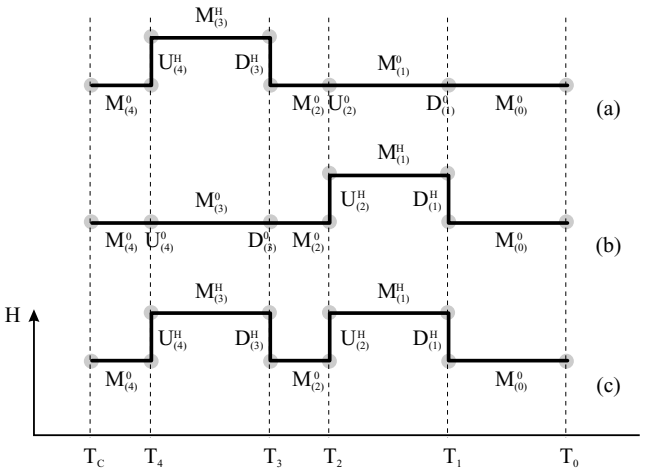

Figure 3. Sketch of the sequence of transition matrices describing the cooling processes for pTRM acquisition. In (a) the pTRM is acquired in the temperature interval $[T_4, T_3]$, in (b) in the interval $[T_2, T_1]$ and in (c) the union of the above intervals is used for pTRM acquisition. In all cases, the lower level represent external zero-field and the upper level a weak field H. Matrices $U_{(j)}^H$ and $D_{(j)}^H$ describe field switching (up and down), while $M_{(j)}^H$ describes cooling in field H from temperature T_{j+1} to T_j.

and discarding higher order terms in H results in

$$w^{(c)} = \frac{W^H_{(c)} - W^0_{(c)}}{H} \approx \frac{W^H_{(a)} - W^0_{(a)}}{H} + \frac{W^H_{(b)} - W^0_{(b)}}{H} = w^{(a)} + w^{(b)} \tag{24}$$

Each $w^{(x)}$ is point antisymmetric, since it is the sum of matrix products, each of which contains exactly one point antisymmetric factor, whilst the other factors are point symmetric.

Eq. (24) provides an additivity law for the first order coefficients of the transition matrices which belong to the pTRM processes in question. To obtain Thellier's law of additivity, (24) must be transformed into a relation between remanences. This can be done by regarding the transition probabilities from state S_0 at T_C into two antisymmetric states S_i and S_{-i} at T_0 by the pTRM$^{(x)}$ process. These probabilities are

$$W^H_{(x)0i} = W^0_{(x)0i} + H w^{(x)}_{0i},$$
$$W^H_{(x)0-i} = W^0_{(x)0i} - H w^{(x)}_{0i}.$$

Since $m(S_{-i}, T_0) = -m(S_i, T_0)$, the weighed contribution $\overline{m}_i$ of states S_i and S_{-i} to the expectation value of the remanence at T_0 is the sum

$$\overline{m}_i = W^H_{(x)0i} m(S_i, T_0) + W^H_{(x)0-i} m(S_{-i}, T_0) = 2H w^{(x)}_{0i} m(S_i, T_0). \tag{25}$$

The expectation value of the total remanence is obtained by summing all contributions $\overline{m}_i$ from antisymmetric pairs.

$$\text{pTRM}^{(x)} = \sum_{i=1}^{N} \overline{m}_i = 2H \sum_{i=1}^{N} w^{(x)}_{0i} m(S_i, T_0). \tag{26}$$

Using (24) one obtains for $H \to 0$ Thellier's law of additivity as

$$\chi_{\text{pTRM}^{(a)}} + \chi_{\text{pTRM}^{(b)}} = \chi_{\text{pTRM}^{(c)}}, \tag{27}$$

where $\chi_{\text{pTRM}^{(x)}} = \frac{d}{dH}\text{pTRM}^{(x)}|_{H=0}$.

Often the additivity law is stated for the special case $T_2 = T_3$ as

$$\chi_{\text{pTRM}(T_1,T_3)} + \chi_{\text{pTRM}(T_3,T_4)} = \chi_{\text{pTRM}(T_1,T_4)}. \tag{28}$$

It has been noted in Ozima & Ozima (1965) that in this case an IRM acquired at T_3 is counted for the left hand side, but not for the right hand side. This was experimentally verified by Levi (1979). Application of the transition matrix method analogous to the above derivation indeed results in the correct relation

$$\chi_{\text{pTRM}(T_1,T_3)} + \chi_{\text{pTRM}(T_3,T_4)} = \chi_{\text{pTRM}(T_1,T_4)} + \chi_{\text{IRM}(T_3)}, \tag{29}$$

where the last term is the susceptibility of an viscous IRM acquired by cooling in zero field to $T_2 = T_3$ switching the field on and off with a residence time of the order of τ_c, and cooling down to T_0 in zero field. There are two slight subtleties related to the transition matrix representation of the viscous IRM process. First, the transition matrix which ensures additivity actually is

$$W^H_{(d)} = M^0_{(0)} D^0_{(1)} M^0_{(1)} U^H_{(3)} D^H_{(3)} M^0_{(3)} U^0_{(4)} M^0_{(4)}, \tag{30}$$

and describes an inverse IRM, because the field is first switched off, and then on. For a real IRM the field switching part of the transition matrix would be $D^H_{(3)}\, U^H_{(3)}$. However, from (23) one recognizes that in first order $D^H_{(3)}$ and $U^H_{(3)}$ commute, and (29) finally turns out to be correct. The second subtlety is that the viscous remanence acquisition due to the intermediate waiting time at T_3 is crucial for the explanation of additivity violations in the limit $H \to 0$. Without viscous remanence, Rayleigh's law states that remanence acquisition in weak fields is proportional to H^2 and thus of second order only.

6 EXTENDED VERSIONS OF THELLIER'S LAW OF ADDITIVITY

Recent experimental investigations of MD TRM revealed that besides the classical additivity law, extended or modified versions are also valid. In Shcherbakov *et al.* (1993) it was found that additivity also holds for an overheated pTRM′, which is generated like a normal pTRM preceded by the cooling process $[T_C, 0] \to [T_0, 0]$ and the subsequent heating $[T_0, 0] \to [T', 0]$, where $T' > T_4$. To describe these processes by transition matrices, the pTRM representations (22) must be modified by a matrix factor

$$C(T') := \left(M^0_{(4)}\right)^{-1} M\left([T_0, 0] \to [T', 0]\right) M\left([T_C, 0] \to [T_0, 0]\right). \tag{31}$$

Thus the process generating pTRM′$^{(x)}$ is represented by $W^H_{(x)}\, C(T')$. Analogous to (24) one obtains for these matrices

$$w^{(c)} C(T') = w^{(a)} C(T') + w^{(b)} C(T'). \tag{32}$$

By checking that the matrices $w^{(x)} C(T')$ are point antisymmetric, it finally can be concluded in correspondence to (27) that

$$\chi_{\text{pTRM}'^{(a)}} + \chi_{\text{pTRM}'^{(b)}} = \chi_{\text{pTRM}'^{(c)}}. \tag{33}$$

A further extension of the additivity law has been reported in Dunlop & Özdemir (2001), where it is stated that even the thermal demagnetization curves of the pTRM$^{(x)}$ are additive. This is true not only for high temperature measurements, but also for the tails tpTRM$^{(x)}(T)$ of pTRM$^{(x)}$ at T, which are obtained by the process $[T_0, 0] \to [T, 0] \to [T_0, 0]$ after pTRM acquisition. Again these modifications of Thellier's law are easily derived in the same fashion as above. The transition matrices of the pTRM representations (22) must be modified by the point symmetric matrix factors

$$E_1(T) := M\left([T_0, 0] \to [T, 0]\right), \tag{34}$$

$$E_2(T) := M\left([T, 0] \to [T_0, 0]\right) M\left([T_0, 0] \to [T, 0]\right) \tag{35}$$

to yield the transition matrices $E_1(T) W^H_{(x)}$ for the high temperature measurements of pTRM$^{(x)}(T)$ or $E_2(T) W^H_{(x)}$ for the tpTRM$^{(x)}$. Exactly as above, (24) assumes the modified form

$$E_k(T) w^{(c)} = E_k(T) w^{(a)} + E_k(T) w^{(b)}, \quad k = 1, 2, \tag{36}$$

which due to the point antisymmetry of each term $E_k(T)\, w^{(x)}$ immediately leads to the additivity laws

$$\chi_{\text{pTRM}^{(a)}(T)} + \chi_{\text{pTRM}^{(b)}(T)} = \chi_{\text{pTRM}^{(c)}(T)}, \tag{37}$$

$$\chi_{\text{tpTRM}^{(a)}(T)} + \chi_{\text{tpTRM}^{(b)}(T)} = \chi_{\text{tpTRM}^{(c)}(T)}. \tag{38}$$

In Dunlop & Özdemir (2001) the validity of this additivity law was interpreted as a consequence of a symmetry of the spectrum of unblocking temperatures with respect to the blocking temperature. However, no such symmetry is needed in the above derivation and therefore additivity is of completely independent nature. A similar conclusion was drawn previously on the basis of a phenomenological model (Fabian 2000). It is evident that the above modification technique can be applied to arbitrary point symmetric modification matrices and thus generates a large class of possible additivity laws.

7 BLOCKING AND UNBLOCKING OF REMANENCE

An essential concept of TRM theories is usually the notion of blocking or unblocking temperatures. Until now this notion didn't occur at all within the presented statistical theory where all state changes

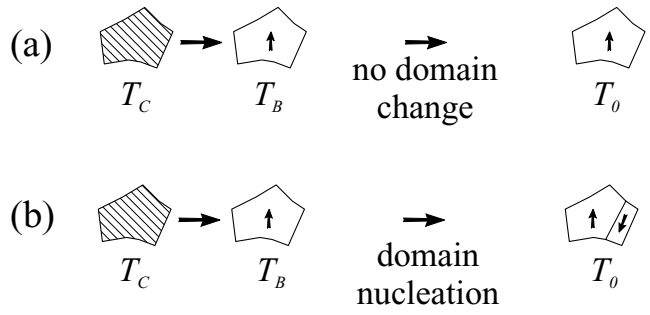

Figure 4. The sketch in (a) illustrates the common definition of the blocking temperature T_B where it is required that no domain changes occur below T_B. The main deficiency of this definition is depicted in (b). Here the critical decision about the remanence at T_0 is made at T_B although nearly certainly some minor domain change occurs between T_B and T_0. According to the common definition, the domain state at T_B in (b) is not blocked.

are solely represented by transition matrices. Here it will be shown that a more abstract concept of blocking and unblocking temperature can be derived from the statistical approach by regarding expectation values of remanence. This concept turns out to be much more appropriate when dealing with transdomain processes.

The most concise definition of the blocking temperature T_B for a cooling SD particle is the temperature at which the expected number of magnetization reversals during the remaining cooling falls below 1 (Stacey & Banerjee 1974). Analogously, one could define the blocking temperature of a domain state S within an MD particle as the temperature at which the probability of a transition away from this state during cooling falls below 1/2 usually. This would regard a state S_i as blocked when during the remaining cooling process it remains unchanged. However, Fig. 4 sketches a typical mechanism by which in MD particles a part of the remanence can be already blocked, even if a change in domain state (e.g. a small domain wall jump) is highly probable to occur at lower temperatures.

To account for changes of the magnetization structure during the whole cooling process, it is more appropriate to consider the blocked remanence at temperature T, which is the expectation value of remanence at T_0 provided that the irreversible magnetization state at T is ρ_T. In Fig. 4 the expectation value of remanence above T_B is 0, while below T_B it is the SD remanence if no transdomain processes occur as in (a) or some smaller value if transdomain effects are present as in (b). In both cases the difference in the expectation value of remanence above and below T_B indicates that a blocking of remanence takes place at T_B. In terms of domain state, this can be regarded as a conditional blocking.

To make this idea precise, it is helpful to introduce a more suggestive notation similar to the Dirac quantum mechanical *bra-ket* formalism. Let $\langle m_T|$ denote the vector with components $m_{T,i} = m(T, S_i)$. This vector acts as a magnetization operator upon the state vectors $|\rho\rangle$ such that if the system at temperature T is in state $|\rho\rangle$, its magnetization is given by $\langle m_T | \rho\rangle$. A temperature change is represented by the transition matrix $M^H_{T,T'} := M([T, H] \rightarrow [T', H])$. The expectation value of remanence at T' after zero field cooling from the state ρ_T at T is

$$\left\langle m_{T'} \left| M^0_{T,T'} \right| \rho_T \right\rangle = \sum_{i,j=-N}^{N} m_{T',i} M^0_{T,T',ij} \rho_{T,j}. \tag{39}$$

It is of interest to study the change of remanence during cooling from some initial state $|\rho^H_T\rangle$ at T to a temperature $T' < T$. Assume that the state $|\rho^H_T\rangle$ has been obtained by cooling from T_C within fields $H(T) \leq H$. It then has the form

$$\left|\rho^H_T\right\rangle = \left|\rho^0_T + H\sigma_T\right\rangle, \tag{40}$$

where $|\sigma_T\rangle$ is a point antisymmetric vector ($\sigma_{T,-i} = -\sigma_{T,i}$). The remanence at T then is given by

$$\left\langle m_T \left| \rho^H_T \right.\right\rangle = \left\langle m_T \left| \rho^0_T + H\sigma_T \right.\right\rangle = H\langle m_T | \sigma_T\rangle. \tag{41}$$

The last equality uses the fact that $|\rho^0_T\rangle$ is point symmetrical and $\langle m_T|$ point antisymmetrical. After cooling to T' the remanence to first order in H is

$$\begin{aligned}\left\langle m_{T'} \left| M^H_{T,T'} \right| \rho^H_T \right\rangle &= \left\langle m_{T'} \left| M^0_{T,T'} + H R_{T,T'} \right| \rho^0_T + H\sigma_T \right\rangle \\ &\approx H\left(\left\langle m_{T'} \left| R_{T,T'} \right| \rho^0_T \right\rangle + \left\langle m_{T'} \left| M^0_{T,T'} \right| \sigma_T \right\rangle\right).\end{aligned} \tag{42}$$

The change in remanence includes three independent effects. First, the operator $\langle m_{T'}|$ is different from $\langle m_T|$ due to different reversible states determining the remanence in $\mathrm{Rev}(S_i)$. Second, a pTRM has been acquired during cooling in field, which is described by $\langle m_{T'} | R_{T,T'} | \rho^0_T\rangle$. Note that this pTRM is independent from the magnetization acquired above T which is represented by $|\sigma_T\rangle$. Third, the previously acquired pTRM is reduced by state changes. This effect is described by $\langle m_{T'} | M^0_{T,T'} | \sigma_T\rangle$ and in first order is independent from the applied field during cooling from T to T'.

To obtain an expression for the weak field blocking potential at temperature T_B one has to consider the difference between two cooling processes

$$T_C \longrightarrow T_B + \Delta T \longrightarrow T_B, \tag{43}$$

where a field H is either switched on or off in the interval $[T_B + \Delta T, T_B]$. Thereby, the blocking potential at T_B can be defined as

$$\begin{aligned}&\overline{\chi}(T_B) \\ &= \lim_{\substack{\Delta T \to 0 \\ H \to 0}} \frac{\left\langle m_{T_B} \left| M^H_{T_B+\Delta T, T_B} \right| \rho^H_{T_B+\Delta T} \right\rangle - \left\langle m_{T_B} \left| M^0_{T_B+\Delta T, T_B} \right| \rho^H_{T_B+\Delta T} \right\rangle}{H\Delta T} \\ &= \left\langle m_{T_B} \left| \alpha_{T_B} \right| \rho^0_{T_B} \right\rangle.\end{aligned} \tag{44}$$

Here α_{TB} is the point antisymmetric linear coefficient of the infinitesimal generator $\mu(T_B, H)$. Thus $\overline{\chi}(T_B)$ is the maximal possible contribution of T_B to the TRM susceptibility at T_0 and (44) shows that it is independent from the details of the cooling process above T_B. The real contribution of the blocked remanence at T_B to the remanence at T_0, is obtained by taking into account the cooling transition

$$T_B \longrightarrow T_0 \tag{45}$$

which leads to

$$\begin{aligned}\overline{\chi}_{T_0}(T_B) &= \lim_{\substack{\Delta T \to 0 \\ H \to 0}} \frac{\left\langle m_{T_0} \left| M^0_{T_B,T_0} M^H_{T_B+\Delta T, T_B} - M^0_{T_B+\Delta T, T_0} \right| \rho^H_{T_B+\Delta T} \right\rangle}{H\Delta T} \\ &= \left\langle m_{T_0} \left| M^0_{T_B,T_0} \alpha_{T_B} \right| \rho^0_{T_B} \right\rangle.\end{aligned} \tag{46}$$

The point symmetric transition matrix $\mathrm{M}^0{}_{T_B,T_0}$ in (46) describes the reduction of the maximal blocking potential (44) by state changes. In a similar way the unblocking of remanence can be investigated by regarding a process

$$T_C \longrightarrow T_B + \Delta T_B \longrightarrow T_B \longrightarrow T_0 \longrightarrow T_{UB} \longrightarrow T_{UB} + \Delta T_{UB},$$

where the field H is switched on only in the step $T_B + \Delta T \longrightarrow T_B$. In the limit $\Delta T_B \rightarrow 0$ the sample carries only a remanence blocked at T_B. The fraction of this remanence, which unblocks at T_{UB} is obtained in the limit $\Delta T_{UB} \rightarrow 0$. Calculations analogous to (44)

yield for the susceptibility of remanence which has been blocked at T_B and unblocks at T_{UB}

$$\chi(T_B, T_{UB}) = \langle m_{T_{UB}} \mid \mu^0_{T_{UB}} M^0_{T_0,T_{UB}} M^0_{T_B,T_0} \alpha_{T_B} \mid \rho^0_{T_B} \rangle . \quad (47)$$

This formula contains a statistical interpretation of the process by which unblocking and blocking temperatures can differ. It traces the average magnetization change of all possible paths of irreversible states which acquire some remanence at T_B and after a sequence of state transition processes lose some remanence at T_{UB}. Here it is important to remember that the occurrence of a state transition is not deterministic. A remanence loss Δm due to a state change $S_j \rightarrow S_i$ may or may not occur during cooling at some temperature $T' < T$. If it didn't occur during cooling, it may just as well occur during heating at the same temperature T' which now is interpreted as an unblocking temperature for the remanence fraction Δm. By summing all possible transition paths with their correct probability the expectation value of remanence change is calculated in (47). The concept of remanence blocking instead of domain state blocking can be naturally extended to cover thermo-viscous processes in MD ensembles where the dependence of thermal demagnetization critically depends upon the initial state before remanence acquisition (Halgedahl 1993).

The above notations $\overline{\chi}$ and $\chi(T_B, T_{UB})$ are chosen to point out the analogy to the phenomenological model of Fabian (2000). However, this similarity is by no means perfect. The statistical theory doesn't imply that TRM acquisition can be described by independent remanence units with fixed T_B and T_{UB}. Therefore it doesn't share the deficiencies of the phenomenological model which result from this assumption. Especially the experimentally found tail of pTRM* (Shcherbakov *et al.* 1993) is compatible with the statistical theory as will be shown in a forthcoming article.

8 DISCUSSION

The statistical concept of probability densities of irreversible states and transition matrices is apt to explain the crucial properties of MD TRM. This concept unifies several previous approaches to use statistical physics for a coherent description of MD TRM. The essence of the renormalization group approach of Ye & Merrill (1995) can be regarded as a calculation of the transition matrix $M([T_C, H] \rightarrow [T_C - \Delta T, H])$ for certain particles. A drawback of the renormalization group method is that further transdomain processes occurring during cooling to T_0 cannot be handled. On the other hand, the kinematic equations proposed by Sugiura (1981), Shcherbakov *et al.* (1993) and Fabian (2000) only deal with an average remanence change and are unable to distinguish between different internal states of the system if these lead to the same remanence. The theory proposed here clearly distinguishes the internal state, represented by $\rho(T)$, the dynamics, represented by M, and the remanence, which is an operator working on ρ. This separation allows the explanation of linearity of MD TRM and very general classes of additivity laws from basic symmetry properties. This reveals that linearity and additivity laws are rooted in fundamental physics. It is not necessary to investigate domain wall properties, diffusive after effects, or symmetries of the unblocking spectrum to explain them. The main intrinsic assumption of the statistical approach is that the involved magnetic energy function actually has sufficient local energy minima with low energy barriers between them to guarantee applicability of Boltzmann statistics.

A problem without a satisfactory solution has always been the connection between heating and cooling processes. On one hand, neither the energy landscape at temperature T, nor the available thermal energy kT depend on the direction of temperature change. On the other hand, experiments show that heating and cooling processes at T behave completely differently and they are usually regarded as being independent from each other. In the statistical theory this puzzle is solved by noting that the transition matrix for heating processes is

$$M([T_1, H] \rightarrow [T_2, H]) = \mathcal{P}_+ \exp\left(\int_{T_1}^{T_2} \mu(\theta, H)\, d\theta\right) \quad (48)$$

and for the cooling process the transition matrix is

$$M([T_2, H] \rightarrow [T_1, H]) = \mathcal{P}_- \exp\left(\int_{T_2}^{T_1} \mu(\theta, H)\, d\theta\right). \quad (49)$$

In both cases the involved infinitesimal generators $\mu(\theta, H)$, representing the energy landscape, are the same, but they are applied in different order (represented by the operators $\mathcal{P}_\pm$, see Appendix A). As they do not commute, the final transition matrices are not inverse to each other and can differ considerably.

An important advantage of the proposed statistical theory is that it can naturally be extended to cover thermo-viscous processes by explicitly including time dependence into the transition matrices. Most parts of the theoretical approach presented here can be extended to this case. In order to calculate time-temperature relations as for single-domain particles (Pullaiah *et al.* 1975; Walton 1980; Worm & Jackson 1988) one has to estimate the relevant energy barrier distributions either by micromagnetic models (Enkin & Williams 1994; Winklhofer *et al.* 1997) or by domain theoretical calculations of wall pinning energies or domain wall nucleation. With respect to palaeomagnetic applications this certainly is the next big obstacle to overcome.

9 CONCLUSIONS

The main result of the previous investigation is the development of a theory which allows derivation of important properties of weak field TRM in MD particle ensembles from basic physical principles. This theory takes into account both, the fundamentally statistical nature of TRM acquisition and deletion, and the occurrence of non-equilibrium magnetization states together with corresponding transdomain processes. The analysis of the statistical theory for weak fields leads to the following conclusions:

(1) Thellier's law of linearity of TRM within weak field holds for generic MD particle ensembles where irreversible state transitions frequently occur during cooling.

(2) Thellier's law of additivity of partial thermoremanences is generally valid for MD particle ensembles in weak external fields. It can neither be invalidated by magnetostatic interaction, nor by full or partial self-reversal. The latter cases only require interpretation of the notion of irreversible state in a sufficiently general fashion to include states of particle ensembles besides single particle domain states. The correction of Ozima and Ozima (1965) to Thellier's law of additivity is necessary when the sum of two pTRMs acquired in adjacent temperature intervals is compared to a single pTRM acquired in the union interval. The method which has been used to prove Thellier's law of additivity applies equally to a wide range of similar additivity properties.

(3) The statistical treatment suggests that blocking and unblocking processes should be understood rather in terms of a change in the expectation value of remanence than in terms of actually blocked

or unblocked domain states. Using the former interpretation the experimentally observed differences between apparent blocking and unblocking temperatures is explained as an effect of the probability distribution for transitions between irreversible magnetization states. The statistical interpretation thereby also resolves the otherwise occurring problem that due to continuous transdomain changes during the cooling process a blocking of domain state may not take place.

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10 APPENDIX A

Part 1

The treatment of the master equation (4) and analogously of (6) is based on results from the theory of linear differential equations in a somewhat unusual form which traces point symmetry and point antisymmetry of the solutions. Therefore, the necessary theorems are stated here in the required form. The presentation is based on Adrianova (1995). Necessary specifications or extensions are given explicitly.

For a differentiable function $\rho : \mathbb{R} \to \mathbb{R}^{2n+1}$ and a continuous matrix function $\mu : \mathbb{R} \to \mathbb{R}^{(2n+1)\times(2n+1)}$, the equation

$$\frac{d}{dT}\rho(T) = \mu(T)\rho(T) \tag{50}$$

is a linear homogeneous system of differential equations. Any set of linearly independent solutions $\rho_{-n}(T), \ldots, \rho_n(T)$ is called a fundamental system of solutions and forms a basis of the solution space. From these, a fundamental matrix $M(T) = (\rho_{-n}(T), \ldots, \rho_n(T))$

can be constructed, which solves the matrix differential equation

$$\frac{d}{dT}M(T) = \mu(T)M(T). \tag{51}$$

Any real solution $M^*(T)$ of (51) can be written as $M^*(T) = C\ M(T)$, where $C \in \mathbb{R}^{(2n+1)\times(2n+1)}$. The matriciant $\Omega^T_{T_0}\,\mu$ is the unique solution of the initial value problem

$$\frac{d}{dT}M(T) = \mu(T)M(T),\ M(T_0) = \mathrm{Id}. \tag{52}$$

Using the matriciant, the general solution of (50) is obtained as

$$\rho(T) = \Omega^T_{T_0}\mu\rho(T_0),$$

for some constant $\rho(T_0) \in \mathbb{R}^{2n+1}$. The matriciant can be expressed in terms of μ as a convergent series

$$\Omega^T_{T_0}\mu = \mathrm{Id} + \int_{T_0}^{T} \mu(\theta_1)\,d\theta_1 + \sum_{k=2}^{\infty}\left(\int_{T_0}^{T}\mu(\theta_1)\,d\theta_1\cdots\int_{T_0}^{\theta_{k-1}}\mu(\theta_k)\,d\theta_k\right). \tag{53}$$

This series expansion appears in several physical contexts like quantum mechanical perturbation theory where it is formally evaluated using linear path ordering operators $\mathcal{P}_+$ or $\mathcal{P}_-$. These operators sort a product over $\mu(\theta_j)$ by a permutation π such that

$$\mathcal{P}_+(\mu(\theta_1)\cdots\mu(\theta_M)) = \mu(\theta_{\pi(1)})\cdots\mu(\theta_{\pi(M)}),\quad \text{with}\quad \theta_{\pi(1)} \geq \theta_{\pi(2)} \geq \cdots \geq \theta_{\pi(M)}, \tag{54}$$

and

$$\mathcal{P}_-(\mu(\theta_1)\cdots\mu(\theta_M)) = \mu(\theta_{\pi(1)})\cdots\mu(\theta_{\pi(M)}),\quad \text{with}\quad \theta_{\pi(1)} \leq \theta_{\pi(2)} \leq \cdots \leq \theta_{\pi(M)}. \tag{55}$$

Using the linearity of $\mathcal{P}_\pm$ one can write

$$\int_{T_0}^{T}\mu(\theta_1)\,d\theta_1\cdots\int_{T_0}^{\theta_{k-1}}\mu(\theta_k)\,d\theta_k = \frac{1}{k!}\mathcal{P}_+\left[\int_{T_0}^{T}\mu(\theta)\,d\theta\right]^k, \tag{56}$$

which finally leads to

$$\Omega^T_{T_0}\mu = \mathcal{P}_+\exp\left[\int_{T_0}^{T}\mu(\theta)\,d\theta\right], \tag{57}$$

whereas the matriciant for cooling is analogously obtained as

$$\Omega^{T_0}_{T}\mu = \mathcal{P}_-\exp\left[-\int_{T_0}^{T}\mu(\theta)\,d\theta\right]. \tag{58}$$

Only if $\mu(T_1)\mu(T_2) = \mu(T_2)\,\mu(T_1)$ for all T_1, T_2 this can be written in terms of the usual matrix exponential

$$\Omega^T_{T_0}\mu = \exp\left(\int_{T_0}^{T}\mu(\theta)\,d\theta\right)$$

and only then $\Omega^{\mathrm{T}}_{T_0}\mu$ and $\Omega^{T_0}_{T}\mu$ are inverse to each other. Since the infinitesimal generators of thermal processes in general cannot be expected to commute, the more general expansion (53) must be used here. Note that in the application of this article the matriciant $\Omega^{\mathrm{T}}_{T_0}\mu$ coincides with the transition matrix $M(T_0 \to T)$.

The influence of a weak field upon the zero-field solution can be taken into account using a theorem on the expansion of the matriciant in powers of a parameter of the infinitesimal generator.

Theorem 1. Let

$$\mu(T,h) = \sum_{k=0}^{\infty}\mu_k(T)h^k,$$

where $\mu_k(T) \in \mathbb{R}^{(2n+1)\times(2n+1)}$ are continuous matrix functions on some interval $T \in J$ and h a real number. Let the above series be absolutely convergent and the norms of its terms converge uniformly for $T \in J$ and $|h| < h_{\max}$. Then for all $\rho_0 \in \mathbb{R}^{2n+1}$ the solution $\rho(T,h)$ of

$$\frac{d}{dT}\rho(T,h) = \mu(T,h)\rho(T,h),\ \rho(T_0,h) = \rho_0 \tag{59}$$

can be expanded in a power series of h that converges absolutely for $T \in J$ and $|h| < h_{\max}$ and whose coefficients are continuous for $T \in J$. Moreover, for all $k \geq 0$ the k-th order approximation of the solution in h depends only on the m-th order terms $\mu_m(T)$ where $m \leq k$. Especially, the first order approximation depends only on $\mu_0(T)$ and $\mu_1(T)$.

The proof of this theorem can be found in Adrianova (1995). The explicit series expansion of the matriciant is

$$M(T,h) = M_0(T) + M_1(T)h^1 + \cdots + M_k(T)h^k + \cdots,$$

where

$$M_0(T) = \Omega^T_{T_0}\mu_0,\ M_k(T) = \textstyle\int_{T_0}^{T}\Omega^T_\theta\mu_0\sum_{i=1}^{k}\mu_i(\theta)M_{k-i}(\theta)\,d\theta,\quad k \geq 1.$$

This implies the stated dependency properties for the k-th order approximations. ∎

In the linear case the point symmetry properties of the matriciant can be predicted from the infinitesimal generator.

Theorem 2. Let $\mu_0(T) \in \mathbb{R}^{(2n+1)\times(2n+1)}$ be a point symmetric and $\mu_1(T) \in \mathbb{R}^{(2n+1)\times(2n+1)}$ a point antisymmetric continuous matrix function on some interval $I \subset \mathbb{R}$. Then for all $h \in \mathbb{R}$

$$\Omega^T_{T_0}(\mu_0 + h\mu_1) = \Omega^T_{T_0}\mu_0 + h\int_{T_0}^{T}\Omega^T_{T'}\mu_0\cdot\mu_1(T')\Omega^{T'}_{T_0}\mu_0\,dT'. \tag{60}$$

This can be written as $M_0(T) + hM_1(T)$, where $M_0(T)$ is point symmetric and $M_1(T)$ is point antisymmetric.

Proof: The representation (60) is a specialization of the general expansion of the previous theorem. From (53) follows, that for point symmetric μ_0 also the matriciant $\Omega^{\mathrm{T}}_{T_0}\mu_0$ is point symmetric. Therefore $M_0(T)$ is point symmetric and the product under the integral in (60) is point antisymmetric, which extends to the integral $M_1(T)$ itself. ∎

Part 2

The following calculation shows that the transition matrix for switching weak fields on within a time interval of the order of τ_{c} in linear approximation is described by

$$M([T,0] \to [T,H]) = I(T,\tau_{\mathrm{c}}) + \beta H, \tag{61}$$

where $I(T,\tau_{\mathrm{c}})$ is the transition matrix for zero-field viscous state changes at temperature T within a time interval τ_{c} and β is a point antisymmetric matrix. The energy barriers between two states S_j and S_i in a weak applied field are given by (10) and (11), even when no temperature change is involved. Switching on a field can be described in various ways, depending on the applied experimental procedure. One simple model is to stop the temperature change, wait for $\tau_{\mathrm{c}}/2$, switch on the field 'instantaneously', wait for $\tau_{\mathrm{c}}/2$ and continue the temperature change. The waiting time is inserted to account for handling. Another model is to describe switching as a field ramp $H(t) = H(1 - (t-t_0)/\tau_{\mathrm{c}})$. Both approaches lead to the same representation of the transition matrix which after calculations analogous to (13)–(15) result in $\beta_{ij} = \frac{1}{2}q(T)\Delta m^0_{ij}I_{ij}(T,\tau_{\mathrm{c}})$ which is point antisymmetric since $I_{ij}(T,\tau_{\mathrm{c}})$ is point symmetric.