A Search for Fluctuation-Dissipation Theorem Violations in Spin Glasses from Susceptibility Data

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Abstract. – We propose an indirect way of studying the fluctuation-dissipation relation in spin-glasses that only uses available susceptibility data. It is based on a dynamic extension of the Parisi-Toulouse approximation and a Curie-Weiss treatment of the average magnetic couplings. We present the results of the analysis of several sets of experimental data obtained from various samples.

Introduction. — The fluctuation-dissipation theorem (FDT) relates the response of a magnetic system to the magnetization correlation function at equilibrium. In its integrated form FDT states that

\[
\chi(t, t_w) = \frac{1}{T}(q_d - C(t, t_w)),
\]

where the response to an applied field \(h\) held constant from a waiting-time \(t_w\) up to \(t\) and the correlation are defined as

\[
\chi(t, t_w) \equiv \delta \langle m(t) \rangle / \delta h|_{h=0} , \quad C(t, t_w) \equiv \langle m(t)m(t_w) \rangle ,
\]

and \(q_d\) is the long-time limit of \(C(t, t).\)

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Glassy systems are out of equilibrium and FDT does not apply, as shown in particular in solvable models with infinite range interactions. Otherwise stated, there are effective temperatures (different from the bath-temperature) at play in aging systems. A simple modification of Eq. (1) consists in proposing that, for large $t_w$, the susceptibility still depends on $t$ and $t_w$ only through $C$, i.e.

$$\chi(t, t_w) = \chi(C(t, t_w))$$  

where $\chi(C)$ is a system-dependent function. The latter may be obtained from a plot of $\chi(t, t_w)$ against $C(t, t_w)$ using $t \geq t_w$ as a parameter. This curve is known analytically for several mean-field spin-glasses such as the Sherrington-Kirkpatrick (SK) model. Models with finite range interactions have been studied numerically by several groups who obtained results that are qualitatively similar to the mean-field ones. These numerical results must however be taken with caution since the times that can be reached in simulations are relatively short.

In principle, $\chi$ and $C$ should be determined experimentally by measuring independently noise correlations and susceptibilities. This procedure has been recently used to investigate FDT violation in structural glasses. For spin-glasses, noise measurements along the lines of the early work of Ref. are under way: their outcome will provide a most stringent test for spin-glass theories.

In this paper, we shall assume that violations of FDT do occur below $T_g$, and propose an indirect method for the determination of the $\chi$ vs $C$ curve using available experimental data. This construction gives a first glimpse of the form of this curve. It is based on some assumptions, notably a dynamic extension of the Parisi-Toulouse (PaT) approximation that hold for some spin-glasses.

We start by noticing that, in all solvable spin-glass models, below $T_g$, $\chi(C)$ is a piecewise function:

$$\chi(C) = \begin{cases} 
\chi_{AG}(C) + \frac{1}{T}(q_d - q) & \text{if } q_d < C < q_0 \\
\chi_{AG}(C) + \frac{1}{T}(q_d - q) & \text{if } q_0 < C < q 
\end{cases}$$  

(FDT regime),

(aging regime),

where the dynamical Edwards-Anderson parameter, $q$, and the minimal correlation in an applied magnetic field $H$, $q_0$, are defined as

$$q = \lim_{t \to \infty} \lim_{t_w \to \infty} C(t, t_w), \quad q_0 = \lim_{t \to \infty} \lim_{t_w \to \infty} C(t, t_w),$$

the latter vanishing in zero applied field. In the SK model, $\chi_{AG}(C)$ is decreasing and has a downwards curvature. Numerical results indicate that, at least within the simulation times, the shape of the curve for the 3D Edwards-Anderson (EA) model is similar.

The dynamical version of the PaT hypothesis (see also Ref.) consists of the following two assertions: (i) $\chi(C)$ is independent of $T$ and $H$ in the aging regime and (ii) $q$ and $q_0$ only depend on $T$ and $H$, respectively. We shall moreover assume that this approximation is good even at finite times (see Discussion).

The near temperature-independence of $\chi(C)$ in the aging regime has been checked numerically for the 4D EA model in Ref. No checks are available for the 3D case. The validity of this approximation for the experimental systems will be discussed below. It will be seen that the PaT approximation allows us to estimate the $C$-dependence of the susceptibility using exclusively response results, thus circumventing the difficulties inherent to noise measurements.

Our strategy is to use data taken under $T$ and $H$ conditions such that the system is at the limit of validity of FDT, i.e. $C(t, t_w) = q$. The point $(q, \chi(q))$ is the intersection between the straight part (FDT regime) and the curved part (aging regime) of $\chi(C)$ (cf. Eq. 3). The
locus of the points obtained varying $T$ and $H$ spans a master curve $\tilde{\chi}(C)$ which, by the PaT hypothesis, is field and temperature independent. The method of construction is explained below and illustrated in Fig. 1.

The susceptibility at the limit of the FDT regime corresponds to:

$$\chi(q) = \lim_{t \to -t_w} \lim_{t_w \to \infty} \chi(t, t_w) = \frac{1}{T}(qd - q).$$  \hspace{1cm} (5)

We have approximated this limit by using susceptibility data of three different types taken from the literature.

**Frequency dependent measurements.**

In ac-susceptibility measurements, a small ac-field of fixed frequency $\omega$ is applied. The in-phase susceptibility $\chi'(\omega, t_w)$ is recorded as a function of temperature. For frequencies in the range $\omega \gg 1$ Hz, the long waiting-time limit $\omega t_w \gg 1$ is approached within the measurement time. Then we can estimate the limit of zero frequency by extrapolation

$$\chi'(0, \infty) \equiv \lim_{\omega \to 0} \lim_{t_w \to \infty} \chi'(\omega, t_w) = \frac{1}{T}(qd - q(T)).$$  \hspace{1cm} (6)

The master curve $\tilde{\chi}(C)$ is obtained by joining the points $\{C = q_d - T \chi'(0, \infty); \tilde{\chi} = \chi'(0, \infty)\}$ using $T$ as parameter.

**Field cooled measurements.** $M_{FC}$ is measured by cooling the sample in a constant magnetic field. Below $T_g$, $\chi_{fc} = dM_{FC}/dH$ rapidly reaches an asymptotic value (see however \cite{10}).

In some spin-glasses like CuMn \cite{12} $\chi_{fc}$ is nearly temperature-independent below $T_g$, $\chi_{fc}(T, H) \sim \chi_{fc}(H)$ as required by PaT. However, this does not hold in most systems for small fields and near $T_g$ where a cusp in $\chi_{fc}$ appears. The $\chi_{fc}$ data may be used where both FDT and PaT hold: on the critical line (assuming there is at least a transient one, an issue discussed below). The parameter is now $H$ and the master curve is spanned by the points $\{C = q_d - T_g \chi_{fc}(H); \tilde{\chi} = \chi_{fc}(H)\}$.

**Zero-field cooled measurements.**

In the absence of a sufficient amount of published ac or fc data, we have resorted to include in the analysis data obtained in a zero-field cooled procedure. The sample is quenched in the absence of a field from above $T_g$ down to some low temperature. After a time $t_w$ (necessary for stabilization of the temperature), a weak magnetic field $H$ is applied and $M_{ZFC}$ is immediately measured. Under typical experimental conditions, the measurement time $t$ is significantly shorter than $t_w$. We shall thus consider that $\chi_{ZFC} = M_{ZFC}/H$ is a good approximation to Eq. (5).

Ideally, the same procedure should be repeated for each measurement temperature. In practice, however, the magnetization $M_{ZFC}$ is measured by increasing the temperature in steps from its initial value. Although the two methods are not strictly equivalent, we believe that the possible differences are of little consequence for our conclusions. Therefore we shall consider that the whole experimental $M_{ZFC}(H)$ curve yields an acceptable approximation to Eq. (5). Support for this point of view is given by a comparison of both ac and ZFC procedures on one sample (see below).

The field-independence of $\chi_{ZFC}$ implied by PaT is in general well verified experimentally except for the largest fields (see, for example, Fig. 1 of the first of Refs. \cite{11}). The master curve is determined as in the ac case.

Before turning to the analysis of the data, we notice that Eq. (5) cannot be applied to experimental data as it stands. Indeed, this equation is only valid for systems in which the exchange coupling averages to zero. In real spin-glasses, however, this average is.
general, finite. This is reflected in the behavior of the high temperature susceptibility that often obeys a Curie-Weiss law. The Curie-Weiss temperature $\theta$ may be a sizeable fraction of $T_g$. Within a mean-field approximation of the average coupling, however, Eq. (3) still holds for the response to the total field (applied plus internal). This amounts to the replacement $\chi \rightarrow \chi\text{MEAS}/(1 + \theta/C \chi\text{MEAS})$, with $\chi\text{MEAS}$ the measured susceptibility and $C$ the Curie constant. In some metallic spin-glasses, like CuMn at low concentration of the magnetic impurity [12], as well as AuFe [13] and AgMn [14], the Curie-Weiss law holds down to the transition temperature. This is not the case in other spin-glasses where, due to progressive clustering, the paramagnetic behaviour deviates from a simple Curie-Weiss law close to the transition. When the Curie-Weiss law holds, a plot of the inverse susceptibility as function of temperature yields the values of $C$ and $\theta$ and it is easy to show that $C = q_d$.

The analysis. — We have analysed data obtained with the methods described above for three metallic systems: CuMn [12] and AuFe [13] for several concentrations, AgMn at 2.6% [14], and two insulating samples CdCr$_{1.7}$In$_{0.3}$S$_4$ [13, 16] and Fe$_{0.5}$Mn$_{0.5}$TiO$_3$ [11].

For CdCr$_{1.7}$In$_{0.3}$S$_4$ we used the $\chi'(\omega, t_w)$ data [16], and extrapolated to zero frequency assuming a power-law decay $\chi'(\omega, \infty) \sim \chi'(0, \infty) + c_1\omega^n$. In the cases of CdCr$_{1.7}$In$_{0.3}$S$_4$ and Fe$_{0.5}$Mn$_{0.5}$TiO$_3$, we also used the FC data to check the consistency of our determination. The susceptibilities $\chi_{zfc}$ were obtained for CuMn, AgMn, AuFe, CdCr$_{1.7}$In$_{0.3}$S$_4$ and Fe$_{0.5}$Mn$_{0.5}$TiO$_3$ using $\chi_{zfc} \approx M_{zfc}/H$. 

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**Fig. 1.** Sketch of the $\chi$ vs $C$ plot. The thick curve represents the master curve $\tilde{\chi}(C)$ that, within the PaT approximation, is temperature and field independent. The thin straight line has a slope $-1/T$ ($T < T_g$) and represents the first line in Eq. (3). The dashed straight line has a slope $-1/T_g(H)$ and joins $(q_d, 0)$ to $(\chi_{fc}(H), q_0(H))$.

**Fig. 2.** $\tilde{\chi}(C)$ plot for CuMn at 1% and 2%. Data are taken from reference [12]. The vertical axis is normalized by the susceptibility at the critical temperature in zero field ($\chi_0$). The horizontal axis is normalized by $q_d = C$. The crosses are numerical results for the 3D EA model [3]. The inset shows the inverse FC and ZFC susceptibilities as functions of temperature.
In order to analyse the field-cooled data, it is necessary to identify the transition temperature in the presence of an applied field. This is done by studying the onset of irreversibilities in the magnetization curves: we defined $T_g$ as the temperature where $M_{irr} = M_{fc} - M_{zfc} = 0$. At high fields, when the relationship between $\chi_{fc}$ and $M_{fc}$ is non-linear, we made polynomial fits of $M_{fc}(H)$ to compute $\chi_{fc}(H) = dM_{fc}/dH$. For high enough fields, $M_{fc}$ is independent of temperature supporting the PaT approximation. However, for some samples, a cusp in the low-field susceptibility may appear near the transition temperature and the determination of a $T$-independent $\chi_{fc}$ becomes ambiguous. In these cases we have used the value $\chi_{fc}$ at the critical temperature in order to ensure consistency with the alternative determination of $\tilde{\chi}(C)$ based on $M_{zfc}$ measurements. On the whole, the construction using $fc$ data is more ambiguous than that using $zfc$ or $ac$ data.

Our analysis is most reliable for CuMn, a system in which the Curie-Weiss law as well as the PaT approximation are very well verified. Figure 2 shows the $\tilde{\chi}(C)$ curve determined using the $zfc$ data of Ref. [12] for two concentrations, 1.08 % and 2.02%. There are no experimental points for $C/q_d > 0.8$ that correspond to rather low temperatures. We know however that $\tilde{\chi}(C)$ tends to zero as $C \rightarrow q_d$ since $\chi_{zfc}(T = 0) = 0$. In addition, the slope $d\tilde{\chi}/dC$ should be infinite at $C = q_d$ so that $q = q_d$ only at $T = 0$. The validity of the hypotheses can be judged by the inset of Fig. 2 where we show the temperature dependence of the inverse susceptibility for the 1.08% compound. A Curie-Weiss law with $\theta \approx 0$ holds accurately for all $T \geq T_g$. The $T$-independence of $\chi_{fc}$ required by the PaT approximation is also well verified below the transition. The same is true for the 2.02% sample.

For comparison, we also show in Fig. 2 the curve $\tilde{\chi}(C)$ for the 3D EA model, at $T = 0.7(< T_g)$ and $H = 0$, obtained numerically in Ref. [3]. The agreement between the numerical results
and the experimental data for the 1.08% sample is remarkable. It may be fortuitous, however, since the results for the 2.02% sample deviate from it. In fact, one must note that $\tilde{\chi}(C)$ is not a universal function. For example, it depends on the details of the Hamiltonian (Heisenberg, Ising and, in general, the level of anisotropy) even at the mean-field level. Thus, there is no reason to expect universality in real systems.

The data for CdCr$_{1.7}$In$_{0.3}$S$_4$ obtained using the three different techniques described above are shown in Fig. 3. It can be noticed that the $fc$ and $ac$ results are very similar. The $zfc$ data are somewhat higher (probably due to the fact that the large $t_w$ condition is not as well full filled as in the other cases), but the agreement with the other determinations remains acceptable. Notice that the $\tilde{\chi}(C)$ curve obtained for this compound is quite different from that corresponding to CuMn.

In Fig. 4 we collect results for all the other samples. As expected, the curves do not fall on a universal curve, but their shape is similar.

**Discussion.**— Finally, let us clarify an important point. In several situations, such as 2D Ising and 3D Heisenberg and, perhaps, 3D Ising spin glasses under a magnetic field, no true spin-glass phase is expected. However, for still relatively long times the system remains below a slowly time-dependent pseudo de Almeida-Thouless (AT) line: it ages and behaves as a true (out of equilibrium) glass with a non-trivial $\chi(C)$ that would eventually become a straight line with slope $-1/T$. In this paper we explored the consequences of the stronger assumption that PaT is a good approximation below the pseudo AT-line if all quantities involved belong to the same epochs.

Another important issue is the asymptotic ($t_w \to \infty$) form of the $\chi_{ag}(C)$ curve. Even if the system never equilibrates, the $\chi_{ag}(C)$ curve may still be a very slowly varying function of $t_w$, eventually reaching a form different from that observed experimentally. We are not in a position to discard this possibility.

It has been recently shown that, under certain hypotheses, the slope of the dynamic $\chi(C)$, for an infinite system in the large-$t_w$ limit coincides with the static $x(q)$ as defined by the probability of overlaps of configurations taken with the Gibbs measure. Since we do not address here the issue as to whether the AT-line and the PaT approximation survive beyond experimental times we cannot make any statements concerning the relation of this dynamical function to the corresponding equilibrium Parisi function.

In conclusion we have presented an approximate determination of the $\tilde{\chi}(C)$ curve characterising the deviations from equilibrium of spin-glasses through the violations of FDT, assuming they exist. This construction does not replace a true determination via simultaneous measurements of susceptibility and noise correlation, as the ones in Ref. [6, 7], but it yields some insight into how this curve might look in reality.

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