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Experimental Evidence of Fluctuation-Dissipation Theorem Violation in a Superspin Glass

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We present the first experimental observation of the fluctuation-dissipation theorem (FDT) violation in an assembly of interacting magnetic nanoparticles in the low temperature superspin glass phase. The magnetic noise is measured with a two-dimension electron gas Hall probe and compared to the out of phase ac susceptibility of the same ferrofluid. For “intermediate” aging times of the order of 1 h, the ratio of the effective temperature T_{eff} to the bath temperature T grows from 1 to 6.5 when T is lowered from T_g to $0.3 T_g$, regardless of the noise frequency. These values are comparable to those measured in an atomic spin glass as well as those calculated for a Heisenberg spin glass.

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During the last two decades, the extension of the FDT to the out-of-equilibrium regime has been the subject of many theoretical and experimental investigations [1–17]. In the “weak ergodicity breaking” scenario [1, 13], it has been shown that the concept of an effective temperature (T_{eff}) [1] that differs from the bath temperature (T) enables the extension of the FDT to the out of equilibrium regime. Therefore, a crucial check of the FDT violation is to determine whether the $T_{\text{eff}} = T$ condition is violated or not. The FDT violation has been investigated in many numerical simulations [13–17], while only a few experimental studies exist; one molecular glass [2], colloids [3–8], polymers [9], one liquid crystal [10] and one spin glass (SG) [11, 12].

Here, we investigate for the first time the FDT violation in an assembly of disordered interacting magnetic nanoparticles in the low temperature superspin glass (SSG) phase. The magnetic nanoparticles suspended in fluid (glycerol) have a single-domain magnetic structure. Therefore, their magnetic moment of $\sim 10^4 \mu_B$ behaves as one large spin, and is called a “superspin”. Since the carrier matrix is frozen, the positions as well as the anisotropy axis orientations of the particles are fixed, and the only remaining degree of freedom is the superspin rotation. The randomness and disorder found in the nanoparticle positions, orientations and sizes lead to magnetically glassy behaviors at low temperatures, including slow dynamics and aging effect, similar to those of atomic SGs, hence these systems are called “superspin glasses” [18–23]. Due to the large magnetic moment, slow

correlation length growth, etc. that makes the observation of magnetic noise with experimental frequency/time range more feasible in a SSG system.

The FDT describes the relation between the power spectrum of fluctuations of an observable, $\delta M(\omega)$ (in our case the observable M is the magnetization) and the imaginary component of the ac susceptibility $\chi''(\omega)$ to the conjugate field [24] in SI units:

$$\langle \delta M(\omega)^2 \rangle = \frac{2k_B T}{\pi V} \left(\frac{\chi''(\omega)}{\mu_0 \omega} \right). \quad (1)$$

Here, $\langle \dots \rangle$ denotes the ensemble average per frequency unit, k_B is the Boltzmann constant, T the temperature, and $\omega = 2\pi f$ (f is the measurement frequency). The departure from equilibrium can be estimated through the fluctuation-dissipation ratio $X(\omega, t_w) = 2k_B T \chi''(\omega, t_w) / (\mu_0 \omega \langle (\delta M)^2 \rangle \pi V)$, or the effective temperature $T_{\text{eff}} = T / X(\omega, t_w)$. X (and T_{eff}) depend on t_w , the waiting time (or the “age”) at T after a temperature quench from above the glass transition temperature of the system. At equilibrium, the FDT gives $X = 1$ and thus $T_{\text{eff}} = T$ while in the aging regime, $X < 1$ and equivalently $T_{\text{eff}} > T$. The effective temperature provides a generic form of FDT in out-of-equilibrium cases as:

$$\langle \delta M(\omega, t_w)^2 \rangle = \frac{2k_B T_{\text{eff}}}{\pi V} \left(\frac{\chi''(\omega, t_w)}{\mu_0 \omega} \right), \quad (2)$$

This equation corresponds to a generalization of the FDT in systems where T_{eff} rather than T acts as temperature, e.g., “weak ergodicity breaking” system. Note that in the $1/\omega \ll t_w$ limit, the quasi-equilibrium regime is reached [1]; that is, the FDT relation is recovered and X equals to 1.

So far, experimental investigations of T_{eff} have been performed on one SG [11, 12], structural glasses [2–9],

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and a liquid crystal [10]. However, due to the difficulty of the fluctuation measurements; i.e., extremely small signals have to be detected, certain claims on the FDT violation remains conflicting [3, 4, 7], suggesting that new measurements are required to help advance this branch of physics.

In this letter, we report the experimental observation of the FDT violation in a frozen ferrofluid in the SSG state via magnetic noise measurements coupled with ac-susceptibility measurements. The ferrofluid used in this experiment is made of maghemite $\gamma\text{Fe}_2\text{O}_3$ nanoparticles dispersed in glycerol with a volume fraction of 15 % [21, 22, 25]. The nanoparticles' average diameter is 8.6 nm and their uni-axial anisotropy energy is $E_a \sim 10^{-20}$ J, obtained from the study of the superparamagnetic relaxation time $\tau = \bar{\tau}_0 \exp(E_a/k_B T)$ with $\bar{\tau}_0 = 10^{-9}$ s for a diluted sample [20], compatible with direct measurements of anisotropy fields [26]. To measure the magnetic noise, a small drop of ferrofluid was deposited directly onto a Hall probe [27, 28] (see inset in Fig. 1). The zero-field-cooled (ZFC) measurements were made well below 190 K, the freezing temperature of glycerol. In a frozen sample, the magnetic moments (superspins) interact with one another through magnetic dipolar interactions leading to a static superspin-glass transition temperature at $T_g \sim 67$ K [21]. The ac susceptibility of the bulk ferrofluid sample (approximately $5 \mu\text{l}$) was measured with a commercial SQUID magnetometer. The magnetic noise was measured with a two-dimension electron gas (2DEG) quantum well Hall sensor (QWHS) based on a pseudomorphic AlGaAs/InGaAs/GaAs heterostructure with a high mobility and a large Hall coefficient R_H ($\sim 800 \Omega/\text{T}$). The QWHS has a nominal sensitive area of $\sim 2 \times 2 \mu\text{m}^2$, located at $d \sim 0.7 \mu\text{m}$ beneath the probe surface (see inset in Fig. 1). The ferrofluid drop of about 7 pl has a diameter $\sim 30 \mu\text{m}$, much larger than the probe sensitive area. We have made use of the spinning current technique which effectively suppresses both the offset and the low frequency background noise of the Hall probe simultaneously [29]. In this method, the directions of the current injection and the Hall voltage detection in Hall cross are continuously switched at a spinning frequency, f_{spin} which is larger than the largest noise frequency of interest. Low frequency background noise ($f < 10$ Hz) suppression is of great importance because the typical time scales involved in the fluctuation dynamics of a SSG system are much larger than 1 s. With $f_{\text{spin}} = 1$ kHz, we achieved a field sensitivity of $\sim 2\text{mG}/\sqrt{\text{Hz}}$ (for $f \sim 0.1$ Hz) for the temperature range between 20 and 85 K; a 10-fold improvement with respect to the sensor sensitivity obtained without this technique. We measured the noise power spectra $S(f)$ of the magnetic field in the Hall probe in two distinct frequency regions; from 0.08 to 0.7 Hz and from 0.8 to 8 Hz. All magnetic noise data of the ferrofluid (except at 85 K) were taken following a temperature quench from 85 K ($= 1.27 T_g$) to the measurement temperatures and a waiting time of 10 minutes for

temperature stabilization. Figure 1 shows an example of such a spectrum, taken at 60 K. $S(f)$ is calculated via $S(f) = \langle [\delta B_z(f)]^2 \rangle = (IR_H)^{-2} \langle (\delta V_H)^2 \rangle$, where δV_H is the fluctuation of the measured Hall voltage, δB_z is the corresponding fluctuation of the (uniform) field B_z perpendicular to the Hall probe and I the injection current. Here the symbol $\langle \dots \rangle$ indicates an averaging over a large data set. Each spectrum was obtained from averaging over 300 and 3000 spectra in the low and high frequency regions, respectively. The aging time t_w of the system is thus this averaging time, which is always of the order of a few 10^3 s. Typical aging experiments using a bulk ferrofluid sample involve t_w 's ranging from a few 10^2 s to several 10^4 s, therefore, such a t_w value is an "intermediate" aging time for a SSG [21].

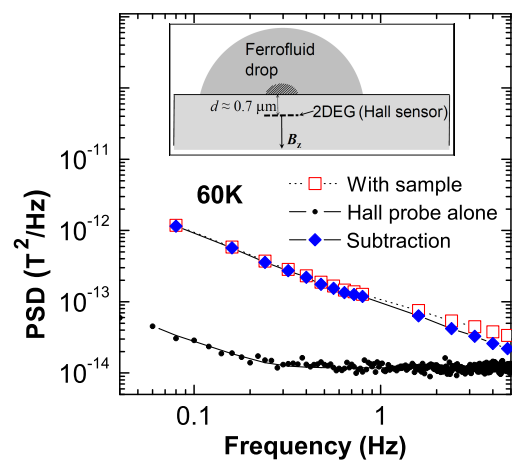


FIG. 1. Noise power spectrum $S(f)$ of the magnetic field due to the frozen ferrofluid (filled lozanges), obtained by subtracting the Hall probe spectrum (dots) from the measured power spectral density (PSD) which contains both of them (open squares) as a function of frequency f , at 60 K in zero applied field. The power spectral density of the magnetic noise due to the sample was larger than that of the bare Hall sensor by factors of about 25 and 2 at 0.1 and 4 Hz, respectively. Inset: Schematic picture of the magnetic noise measurement experiment. Because of its geometry and of the $1/r^4$ dependence of the dipolar field fluctuation, the magnetic noise measured in the probe comes mainly from a volume located in front of the 2DEG [26] (hatched area).

Figure 2 shows the imaginary part of the ac magnetic susceptibility $\chi''(f, T)$ of a bulk sample as a function of Sf/T at $f = 0.08, 0.8, 4$ Hz. $\chi''(f, T)$ at each temperatures was measured with the aging time t_w of 1 hour after the temperature quench from 85 K. We found that all data points belonging to the temperature range $T > T_g = 67$ K are aligned along a common straight line; i.e., $\chi'' \propto Sf/T$. The solid straight line in Fig. 2 is the best fit to these data points for $T = T_g$ for all three frequencies. This linear relationship is independent on f ,

indicating that the FDT holds between the two quantities in this T range according to Eq. 1. The data points deviate from the straight line starting from the maximum value of χ'' occurring near $T = T_g$ and downwards in temperature. Figure 3 shows the temperature dependencies of χ'' and Sf/T (same data as in Fig. 2). The relative normalization of the two vertical scales, χ'' and Sf/T , is given by the slope of the straight line found in Fig. 2. As expected, χ'' and Sf/T superpose in the high temperature region above T_g , while they separate below T_g . Both the deviation from the linear relation and the separation of the normalized χ'' and Sf/T below T_g indicate a clear FDT violation. The value of the

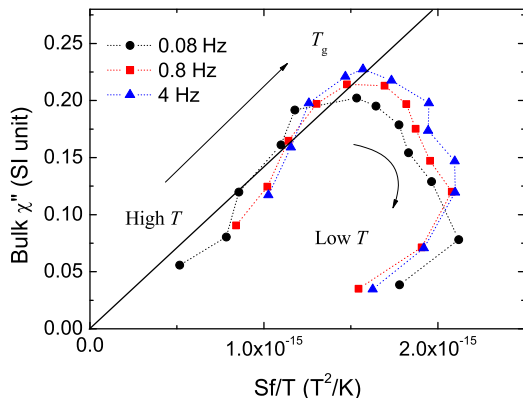


FIG. 2. $\chi''(f, T)$ of bulk sample as a function of $S(f, T)f/T$ for frequencies, 0.08, 0.8 and 4 Hz. Each data point corresponds to χ'' and S measurements at a given bath temperature T and frequency f . The solid straight line indicates the linear relation in the high temperature region above T_g .

slope, $\chi''/(Sf/T) = (1.4 \pm 0.2) \times 10^{14}$ [K/T^2] in the high temperature region (see Fig. 2) is determined by the effective volume V_{eff} of ferrofluid that contributes to the magnetic noise measurement [27] and by the magnitude of the magnetic field induced by the ferrofluid in the Hall probe. Because of the sample geometry and of the $1/r^4$ [27] dependence of the variance of the dipolar field $\langle(\delta\bar{B}_z)^2\rangle$, where \bar{B}_z is the average of B_z induced by the sample over the probe sensitive area, V_{eff} is confined within a volume close to the sensor surface (see inset of Fig. 1). To check the quantitative consistency of the above analysis, we have estimated the slope value independently. Depth investigations of the response of a Hall cross to an inhomogeneous perpendicular field B_z have revealed that this response is proportional to the average of B_z over the effective area a_{eff} of the probe which is about twice the junction area, i.e., $a_{\text{eff}} = 2w^2$ (w being the width of the cross arms) [30]. We evaluated numerically the variance $\langle(\delta\bar{B}_z)^2\rangle$ with B_z being the sum of contributions from elementary volumes $d^3\mathbf{r}$ of the sample, each having a magnetic moment variance given by FDT; that is $(2k_B T \chi''/\pi\mu_0\omega)d^3\mathbf{r}$. The calculated slope

is $(0.7 \pm 0.25) \times 10^{14}$ [K/T^2]. The uncertainty comes mainly from that of the response function of the probe, which is partly due to the uncertainty in the actual value of w ($1 \mu\text{m} < w < 2 \mu\text{m}$) caused by the edge depletion effect. Another source of uncertainty comes from the fact that the effect of averaging B_z over the probe area has been evaluated using a Monte-Carlo simulation to which some simplifying assumptions were made, i.e., independent superspins, square probe area, etc.). Despite these elements taken into account, the measured and calculated slope values are close to each other, lending the creditability of our results.

Below the SSG transition temperature T_g , the system is in an out-of-equilibrium state. Therefore it should not and does not obey the equilibrium FDT relation. We can now estimate the effective temperature T_{eff} as evoked above from the FDR ratio of χ'' to Sf/T (see Eq. 2). The inset in Fig. 3 shows the temperature dependence of T_{eff}/T obtained at the three experimental frequencies. T_{eff}/T increases monotonically when T decreases, starting from 1 around T_g , to 6.5 at $0.3T_g$ ($= 20$ K) regardless of the frequency. The values of T_{eff}/T are of the same order as those reported in the experimental study of an atomic SG, $T_{\text{eff}}/T = 2.8 - 5.3$ [12] and in a Monte-Carlo simulation on a Heisenberg SG, $T_{\text{eff}}/T = 2 - 10$ [17].

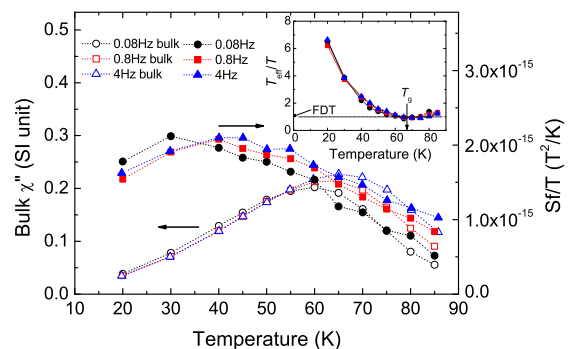


FIG. 3. Temperature dependent χ'' of bulk sample (open symbols) and Sf/T (filled symbols) at frequencies; 0.08, 0.8 and 4 Hz. The relative normalization of the two vertical scales corresponding to χ'' and Sf/T is given by the slope of the straight line in Figure 2. Inset: The temperature dependence of T_{eff}/T at $f = 0.08, 0.8$ and 4 Hz. The dashed line corresponds to the FDT relation, i.e., $T_{\text{eff}}/T = 1$.

The fact that we obtain $T_{\text{eff}} > T$ for $T < T_g$ suggests that the system is in the aging regime, and not in the so-called quasi-equilibrium regime [1]. The latter corresponds to observation times $t_{\text{obs}} = 2\pi/\omega$ much smaller than the aging time t_w . Here, $t_{\text{obs}} \sim 1$ s is rather short compared with $t_w \sim 10^3$ s. Therefore, one may expect the system to be in quasi-equilibrium and consequently, the FDT to hold. Our experimental observation clearly states otherwise. In the domain growth picture of SG's [31], the condition for the quasi-equilibrium regime

is not only that $t_{\text{obs}} \ll t_w$, but also that $\ln(t_{\text{obs}}/\tau_0) \ll \ln(t_w/\tau_0)$, where $\tau_0 = \bar{\tau}_0 \exp(E_a/k_B T_g)$ is a microscopic flip time of a single superspin. $\ln(t_{\text{obs}}/\tau_0)$ and $\ln(t_w/\tau_0)$ are ~ 9 and ~ 16 for $t_{\text{obs}} \sim 1$ s and $t_w \sim 10^3$ s, respectively with $\tau_0 \sim 10^{-4}$ s. Therefore, the condition $\ln(t_{\text{obs}}/\tau_0) \ll \ln(t_w/\tau_0)$ is not satisfied. This view is further supported by the correlation length ξ evaluation in the same system under similar experimental conditions [21]. Assuming $\xi/\xi_0 = (t/\tau_0)^{\alpha T/T_g}$ as in [21] with $\tau_0 = 10^{-4}$ s, $\alpha = 0.15$ and $T = 0.7T_g$, we estimate the ξ , values to be $2.6\xi_0$ at $t_w = 1$ s and $5.4\xi_0$ at $t_w = 10^3$ s. Note that ξ_0 is a unit length scale; i.e., of the order of 13 nm, the average distance between two neighboring nanoparticles. The ratio of the length scales between the two time scales is only 2. This suggests that the growth of a correlated domain during t_{obs} is sufficiently large to include the domain walls depicted in [31], enabling the out-of-equilibrium dynamics to be already observed. It is worth mentioning here that FDT violations for short observation times, $t_{\text{obs}} \ll t_w$ have also been observed in structural glasses [3, 4, 8].

In conclusion, we observed a clear violation of FDT in the out-of-equilibrium, aging SSG state of a frozen ferrofluid through magnetic noise measurements. For an aging time of about 1 hour, the extracted effective temperature-to-bath temperature ratio, T_{eff}/T , increases by a factor of 6.5 when T decreases from T_g to $0.3T_g$. Such values are of the order of those found in an atomic SG and in a numerical simulation of a Heisenberg SG. T_{eff}/T quantifies the departure from equilibrium and should depend on the age of a given out of equilibrium system. More investigations are needed to elucidate aging time dependence of T_{eff} . The FDT violation in magnetic nanoparticle systems with dipolar interaction has not so far been treated numerically, thus comparisons with such calculation results is much desired.

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