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

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We present the experimental observation of the fluctuation-dissipation theorem 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 fluctuation-dissipation theorem (FDT) to the out-of-equilibrium regime has been the subject of many theoretical and experimental investigations [1–21]. In the "weak ergodicity breaking" scenario [1,3], it has been shown that the concept of an effective temperature (T_{eff}) [3] that differs from the bath temperature (T) enables the extension of the FDT to the out-of-equilibrium regime. The FDT violation has been investigated in several numerical simulations [1,2,5–7,22,23], while experimental studies are rather scarce: they concern one molecular glass [8], colloids [9,12,15–17,20], polymers [13,14,21], one liquid crystal [18], and one spin glass (SG) [10,11]. On the other hand, the absence of FDT violation is reported in colloids [17,19] and in a magnetic nanoparticle system [24,25]. Thus, the systems and the conditions in which the FDT is violated still represent an open question.

Here, we investigate the FDT violation in an out-of-equilibrium superspin-glass (SSG) system. 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." Once 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 effects, similar to those of atomic SGs; hence these systems are called "superspin glasses" [24,26–31]. Because of the large magnetic moment, slow correlation length growth, etc., the observation of magnetic noise within experimental frequency or time range becomes more feasible in a SSG system. Furthermore, the much slower microscopic time scale in SSG than that in SG can help to fill the large time scale gap between the computer simulations and experiments.

The FDT describes the relation between the power spectrum of fluctuations of an observable, $\delta M(\omega)$ (here M is the magnetization) and the imaginary component of the ac susceptibility $\chi''(\omega)$ to the conjugate field [32]:

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

Here, $\langle \cdots \rangle$ 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 $X(\omega, t_w) = 2k_B T \chi''/(\mu_0 \omega \langle (\delta M)^2 \rangle \pi V)$, or the effective temperature $T_{\mathrm{eff}} = T/X(\omega, t_w)$. 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 $T_{\mathrm{eff}} = T$ while in the aging regime, $X < 1$ and equivalently, $T_{\mathrm{eff}} > T$. The effective temperature provides a generalized form of FDT in out-of-equilibrium cases as

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

where T_{eff} rather than T acts as the system temperature, e.g., "weak ergodicity breaking" system. Note that in the $1/\omega \ll t_w$ limit, the quasiequilibrium regime is reached [3]; that is, the FDT relation is recovered and $X = 1$.

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 here is made of maghemite γFe_2O_3 nanoparticles of average diameter 8.6 nm, dispersed in glycerol with a volume fraction $\phi \sim 15\%$ in which the SSG state is observed [29,30,33,34], in agreement with Refs. [26,27] where the ϕ dependent SSG transition is tested with ϵ-Fe_3N ferrofluids. Indeed the dipolar interaction energy over anisotropy energy $\sim \mu_0 m_s^2 V_{\rm np}\phi/E_a$ (m_s, $V_{\rm np}$ particle magnetization and volume) is here close to that of SSG sample with $\phi \sim 2\%$ in Ref. [26]. Particle uniaxial anisotropy energy $E_a \sim 10^{-20}$ J (as in Ref. [26]), is obtained from the superparamagnetic relaxation time of a diluted sample, $\tau = \bar{\tau}_0 \exp(E_a/k_B T)$ with $\bar{\tau}_0 = 10^{-9}$ s [28], compatible with direct anisotropy field measurements [35]. To measure the magnetic noise, a small drop of ferrofluid was deposited directly onto a Hall probe [36,37] (see inset in Fig. 1). All 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 dipolar interactions leading to a static superspin-glass transition at $T_g \sim 67$ K [29]. The ac susceptibility of the bulk ferrofluid sample (approximately 5 μl) 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 pseudomorphic AlGaAs/InGaAs/GaAs heterostructure with a high mobility and a large Hall coefficient $R_{\rm H}$ ($\sim 800\ \Omega$/T). The QWHS has a nominal sensitive area of $\sim 2 \times 2\ \mu{\rm m}^2$, located at $d \sim 0.7\ \mu$m beneath the probe surface (see inset in Fig. 1). The ferrofluid drop of about 7 pl has a diameter $\sim 30\ \mu$m, much larger than the probe sensitive area.

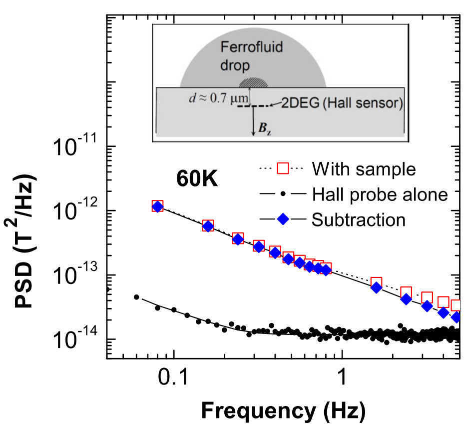

FIG. 1 (color online). Noise power spectrum $S(f)$ of the magnetic field due to the frozen ferrofluid (filled diamonds), obtained by subtracting the Hall probe only spectrum (dots) from the total power spectral density (PSD) (open squares) as a function of frequency f, at 60 K in zero applied field. 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 setup. The magnetic noise measured in the probe comes mainly from that part of the drop located in front of the 2DEG [36], indicated by the dark shaded region (see text).

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 [38]. In this method, the directions of the current injection and the Hall voltage detection in Hall cross are continuously switched at a spinning frequency $f_{\rm spin}$ 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 $f_{\rm spin} = 1$ kHz, we achieved a field sensitivity of 2×10^{-7} T/$\sqrt{\rm Hz}$ (for $f \sim 0.1$ Hz) for the temperature range between 20 and 85 K, a tenfold improvement with respect to the sensor sensitivity obtained without this technique. The noise power spectra $S(f)$ of the magnetic field were measured 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 min for temperature stabilization. Figure 1 shows an example of such a spectrum, taken at 60 K. $S(f)$ is calculated via $S(f) = \langle [\delta B_z(f)]^2 \rangle = (IR_{\rm H})^{-2} \langle (\delta V_{\rm H})^2 \rangle$, where $\delta V_{\rm H}$ 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 $\langle \cdots \rangle$ 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, here of the order of a few 10^3 s. This is an "intermediate" waiting time used in typical aging experiments on bulk ferrofluid SSG samples where t_w's range from a few 10^2 s to several 10^4 s [29].

Figure 2 shows the imaginary part of the ac magnetic susceptibility $\chi''(f, T)$ of a bulk sample as a function of

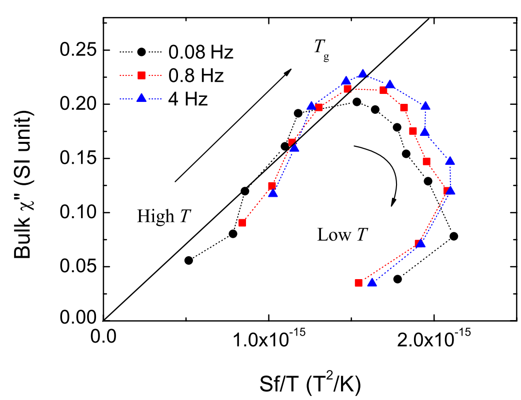

FIG. 2 (color online). $\chi''(f, T)$ of bulk sample as a function of $S(f, T)f/T$ for frequencies, 0.08, 0.8, and 4 Hz. Each data point corresponds to χ'' and S measurements at a given bath temperature T and frequency f. The solid straight line indicates the linear relation in the high temperature region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

Sf/T at $f = 0.08$, 0.8, 4 Hz. $\chi''(f, T)$ at each temperature was measured with the aging time t_w of 1 h after the temperature quench from 85 K. We found that all data points collected above $T_g = 67$ 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 of 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 can be seen from the figure, χ'' and Sf/T superpose in the high temperature region above T_g, while they separate below T_g. The deviation from the linear relation and the separation of the normalized χ'' and $Sf = T$ below T_g indicate a clear departure from FDT. The slope value, $\chi''/(Sf/T) = (1.4 \pm 0.2) \times 10^{14}$ [K/T^2] in the high temperature region (see Fig. 2) is determined by the effective volume $V_{\rm eff}$ of ferrofluid that contributes to the magnetic noise measurement [36] and by the magnitude of the magnetic field induced by the ferrofluid in the Hall probe. Because of the sample geometry and of the $1/r^4$ [36] dependence of the dipolar field variance $\langle(\delta\bar{B}_z)^2\rangle$, where $\bar{B}_z$ is the average of B_z induced by the sample over the probe sensitive area, $V_{\rm eff}$ 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. In 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 $a_{\rm eff}$ of the probe which is about twice the junction area, i.e., $a_{\rm eff} = 2w^2$ (w being the width of the cross arms) [39]. We evaluated numerically the variance $\langle(\delta\bar{B}_z)^2\rangle$ with B_z being the sum of contributions from elementary volumes $d^3\boldsymbol{r}$ of the sample, each having a magnetic moment variance given by FDT, that is $(2k_BT\chi''/\pi\mu_0\omega)d^3\boldsymbol{r}$. 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 true 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 credibility to our results.

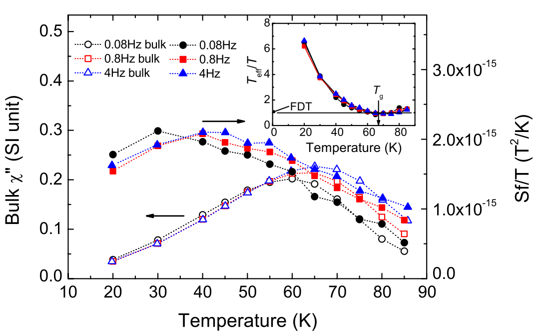

FIG. 3 (color online). Temperature dependent χ'' of bulk sample (open symbols) and Sf/T (filled symbols) at frequencies 0.08, 0.8, and 4 Hz. The relative normalization of the two vertical scales corresponding to χ'' and Sf/T is given by the slope of the straight line in Fig. 2. Inset: The temperature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

Below the SSG transition temperature T_g, where the system is in an out-of-equilibrium state, we have witnessed a departure from the equilibrium FDT relation. We now estimate the effective temperature $T_{\rm eff}$ as evoked above from the FDT ratio of χ'' to Sf/T [see Eq. (2)]. The inset in Fig. 3 shows the temperature dependence of $T_{\rm eff}/T$ obtained at 0.08, 0.8, and 4 Hz. $T_{\rm eff}/T$ 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 $T_{\rm eff}/T$ are of the same order as those reported in the experimental study of an atomic SG, $T_{\rm eff}/T = 2.8 - 5.3$ [11] and in a Monte Carlo simulation on a Heisenberg SG, $T_{\rm eff}/T = 2 - 10$ [7].

The observation of $T_{\rm eff} > T$ suggests that the system is in the aging regime, i.e., not in the so-called quasiequilibrium regime [3] where observation times $t_{\rm obs} = 2\pi/\omega$ are much smaller than the aging time t_w. Here, $t_{\rm obs} \sim 1$ s is rather short compared to $t_w \sim 10^3$ s, corresponding to $t_{\rm obs}/t_w \sim 10^{-3}$. Violations of FDT have been observed experimentally for very low values of $t_{\rm obs}/t_w$: $10^{-7} - 10^{-4}$ in a molecular glass [8], $10^{-5} - 10^{-3}$ in polymer glasses [13,14], and $10^{-7} - 10^{-4}$ in colloidal glasses [9,12,20]. Furthermore, in those experimental systems, $T_{\rm eff}$ does not rapidly approach the bath temperature T with waiting time t_w. Through numerical simulations on domain growth systems [5], the breaching of the quasiequilibrium state depends on the system itself and on the two time scales ($t_{\rm obs}$ and t_w) separately rather than on $t_{\rm obs}/t_w$ [40]. Similar conclusions were drawn in SG simulations [22,23]. In an interacting magnetic nanoparticle SSG system similar to ours, the FDT remained valid for $t_{\rm obs}/t_w < 10^{-5}$ [25]. Thus, it is tempting to conjecture that the limit between the two regimes lie somewhere between $t_{\rm obs}/t_w = 10^{-5}$ and 10^{-3}. However, one must be careful because the differences between the two systems (particle sizes, concentrations, etc.) and their experimental conditions (measurement techniques, temperature quench protocol, etc.) do not allow direct comparison between the two studies.

Comparing the SSG and SG systems, we note that the interaction between superspins is of the long range dipolar type whereas between atomic spins, it is of the short range exchange type [10,11,23]. Thus far, a large scale dynamical simulation on nanoparticle systems with random anisotropy has not been investigated in terms of the FDT relation. Comparisons of experimental data to such simulation result will be very interesting.

In conclusion, we have presented experimental evidence of FDT violation in the out-of-equilibrium, aging SSG state of a frozen ferrofluid through magnetic noise measurements. For an aging time of about 1 h, the extracted effective temperature (normalized to the bath temperature), increases by a factor of 6.5 when T decreases from T_g to 0.3 T_g. Such values are of the order of those found in an atomic SG [11] and in a numerical simulation of a Heisenberg SG [7]. More investigations are needed to elucidate aging time dependence of T_{eff} as well as the particle system dependence with different interaction strengths and anisotropy energies.

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