ARTICLE IN PRESS

Journal of Magnetism and Magnetic Materials ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

# Reprint of: Out-of-equilibrium dynamics in superspin glass state of strongly interacting magnetic nanoparticle assemblies

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ARTICLE INFO

*Article history:*
Received 10 September 2013
Received in revised form
2 December 2013
Available online 17 December 2013

*Keywords:*
Superspin glass
Out-of-equilibrium dynamics
Magnetic nanoparticles

ABSTRACT

Interacting magnetic nanoparticles display a wide variety of magnetic behaviors ranging from modified superparamagnetism, superspin glass to possibly, superferromagnetism. The superspin glass state is described by its slow and out-of-equilibrium magnetic behaviors akin to those found in atomic spin glasses. In this article, recent experimental findings on superspin correlation length growth and the violation of the fluctuation-dissipation theorem obtained in concentrated frozen ferrofluids are presented to illustrate certain out-of-equilibrium dynamics behavior in superspin glasses.

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## 1. Introduction

Magnetic nanoparticles (np) are, as the name suggests, a class of nanometric particles made of magnetic elements such as iron, nickel and cobalt and their alloys. A quick search on "magnetic nanoparticles+research" reveals a plethora of current research efforts involving magnetic np's for their potential (and some current) use in biomedicine [1], magnetic resonance imaging [2], tomographic imaging [3], data storage [4], nanofluids [5], *etc*. While their unique and tunable physical properties (most generally that of superparamagnetism) make them attractive for technological applications, the np magnetism by itself has also been a focus of active fundamental research since the original works by Néel [6], Stoner and Wolfarth [7] in the 1940s.

Within a single-domained nanoparticle, all atomic spins are aligned in the same direction and thus it can be considered as a small permanent magnet with a large magnetic moment, typically in the order of $10^3$–$10^5$ $\mu_B$, where $\mu_B$ is the Bohr magneton [8]. The energy that holds the spins aligned together is called "anisotropy energy" and the magnetization reversal of one particle requires the collective rotation of *all* atomic spins by overcoming the anisotropy energy barrier.

If nanoparticles are widely spaced and hence non-interacting, their magnetization rotation dynamics is governed solely by thermal agitation, each behaving like a paramagnetic atom but with a much larger magnetic moment (also known as superspins) leading to the phenomenon known as *superparamagnetism*. In an assembly of concentrated yet isolated particles (not touching), the magnetic properties can be greatly influenced by the dipolar interaction energy among neighboring particles [9,10]. Dipolar interactions modify the effective energy barrier height of individual particles; *i.e.*, the reversal of one superspin can change the energy barriers of surrounding nanoparticles. In strongly interacting nanoparticle systems, low temperature collective states are observed. These collective states, now called *superspin glasses*, show many magnetic features that are common among atomic spin glasses [11–25].

"Spin glass (SG)" and "superspin glass (SSG)" refer to metastable magnetic states created by quenched (frozen) and randomly interacting magnetic moments [26–28]. In reality, such systems are produced by random inclusion of magnetic impurities in a non-magnetic medium (in SG), or magnetic nanoparticles in a solid matrix such as a frozen fluid or a solid material (in SSG). The randomness induces competing interactions (frustrations) among magnetic moments such that it is difficult to find a global (super)spin configuration that minimizes the system's energy, resulting in a multitude of highly degenerate ground states. Therefore, the (super)spin dynamics of SG's and SSG's are always out-of-equilibrium; *i.e.*, their magnetization relaxes slowly while neighboring (super)spins form 'correlated zones' whose size grows forever in search of a true ground state. SG experiments revealed a large collection of peculiar dynamic behaviors that cannot be explained by one universal model. Generally, SG behaviors are interpreted within the framework of two models. One is the Parisi's solution to the Sherrington–Kirkpatrick model, where the low temperature SG state consists of "infinitely many pure thermodynamic states" [29–32]. The other is the "droplet" model introduced by Fisher and Huse,

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DOI of original article: http://dx.doi.org/10.1016/j.jmmm.2013.12.018

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http://dx.doi.org/10.1016/j.jmmm.2014.05.045
0304-8853/© 2014 Published by Elsevier B.V.

Please cite this article as: S. Nakamae, Journal of Magnetism and Magnetic Materials (2014), http://dx.doi.org/10.1016/j.jmmm.2014.05.045

based on the domain wall renormalization concepts. Here, there is only a single-pair of spin-flip-reversed pure states at low temperature in any finite dimension [33–37].

Despite some fundamental differences between atomic SG's and nanoparticle SSG's; *e.g.*, short-range exchange (SG) *vs.* long-range dipolar (SSG) interactions, theoretical models developed for atomic SG's have so far succeeded in describing many aspects of SSG dynamics. From the experimental point-of-view, interacting magnetic np systems present certain advantages; *e.g.*, slower superspin fluctuations and larger magnetic moments, which make them particularly advantageous for the investigation of existing theoretical models.

Here, recent experimental studies on the out-of-equilibrium SSG dynamic behaviors in concentrated frozen ferrofluid samples made of maghemite nanoparticles dispersed in glycerin are presented; *i.e.*, (1) the dynamic superspin correlation length growth and (2) the violation of the fluctuation-dissipation theorem (FDT). For the former study two types of samples were examined; one in which anisotropy-axis of np's are randomly distributed and the other where anisotropy-axis were all aligned in parallel. These samples are denoted as 'random and 'aligned', respectively.

## 2. Out-of-equilibrium behaviors of superspin glasses

### 2.1. The onset of SSG state

When studying the magnetic property of a magnetic nanoparticle assembly, it is most instructive to start with the so-called "ZFC/FC measurements" as illustrated in Fig. 1 (left panel). The FC curve corresponds to the magnetization measured after the sample is cooled in the presence of a small magnetic field *H*, while the ZFC curve is obtained after cooling in zero-field and applying *H* at the lowest temperature. It should be noted that the separation between the ZFC and FC curves alone is not a signature of a low-temperature SSG state; rather, it simply indicates the existence of irreversibility. As it is well known, non-interacting superparamagnetic nanoparticles also exhibit similar splitting between the ZFC and FC curves due to the blocking of individual superspins without having any collective state. That being said, the apparent flatness, or a slight decrease in the FC curve below the freezing temperature is suggestive of a collective behavior. Thus the ZFC/FC measurements have become a staple initial test when studying *could-be* superspin glass samples.

A commonly used "test" to distinguish between a blocked SPM state from an SSG state is the frequency dependent magnetic susceptibility ($\chi$) measurements. When particles are non-interacting, the ac susceptibility $\chi(T, \omega)$ peak follows an Arrhenius law $\tau=\tau_0\exp(E_a/k_BT)$, where $\tau$ is the inverse of the measurement frequency $\omega$, $\tau_0$ is a microscopic limiting relaxation time, (typically $\sim 10^{-9}$ s) and $E_a$ is the anisotropy energy of individual nanoparticles. Applying this law to concentrated nanoparticle systems, one generally obtains unphysically small $\tau_0$ values. Instead, the frequency dependent $\chi(\omega, T)$ peak is best described by a critical-law of the form

$$\tau(T)/\tau_o=((T-T_g)/T_g)^{-zv} \qquad (1)$$

here $zv$ the dynamic exponent and $T_g$ the glass transition temperature at $\omega=0$. In the concentrated frozen ferrofluid samples used in the following studies, $zv$ values were between 5 and 12 [38], similar to those found in atomic spin glasses [39].

### 2.2. Dynamic superspin correlation length growth

If an SSG sample is zero-field cooled quickly to a certain temperature $T<T_g$ and then a small magnetic field, *H* is applied, its magnetization will first jump to the ZFC(*T*) value then slowly increase toward the equilibrium value; *i.e.*, ZFC $(t, T)\rightarrow$FC(*T*) (see Fig. 1 left panel). Conversely, if the sample is cooled in *H* to $T<T_g$ and subsequently the field is turned off, the magnetization will decrease. The latter effect is called the "thermo-remanent" magnetization relaxation (TRM(*t*, *T*)). In spin glasses, it has been demonstrated that ZFC(*T*)+TRM(*t*, *T*)=FC(*T*) and the same relation also appears to hold in superspin glasses. It is in this TRM region (shaded in blue in Fig. 1 (left) between the FC(*T*) and ZFC(*T*) curves) where slow, glassy behavior is observed in spin glasses and superspin glasses.

One important feature of the out-of-equilibrium dynamics of SSG is the "ageing" effect (relaxation) that takes place at all timescales (from the microscopic to possibly geological time scales). This occurs due to the disordered and frustrated nature of interactions that prohibits superspins from quickly establishing a unique ground state. Rather, superspins form locally "correlated zones" whose size grows steadily with time. In SSG's (and SG, of course), this effect can be observed in their magnetization relaxation (ZFC(*t*) and TRM(*t*), see above).

In the ZFC measurement protocol, a sample is cooled from a temperature well above $T_g$, to a measuring temperature, $T_m<T_g$ in

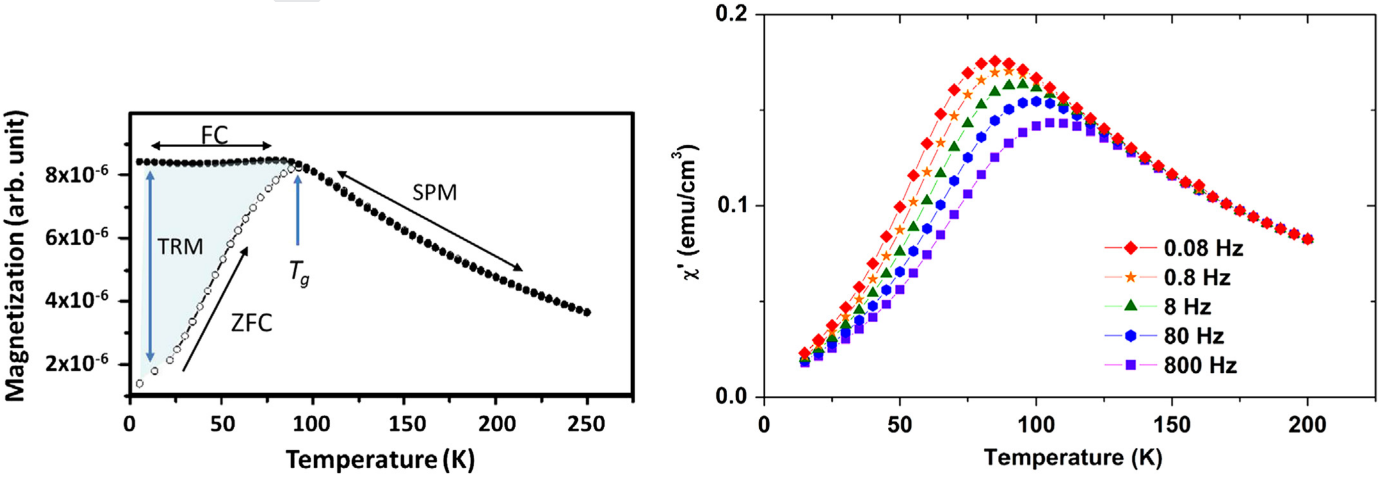

**Fig. 1.** (Left): FC (filled circles) and ZFC (open circles) magnetization *vs.* temperature curves at 0.5 G, measured on a concentrated (35%) ferrofluid sample ($\gamma$-Fe$_2$O$_3$ nanoparticles suspended in water) [23]. The blue-shaded area describes the *out-of-equilibrium* zone. (Right): Real part of AC susceptibility as a function of temperature. The sample used: $\gamma$-Fe$_2$O$_3$ ferrofluid in glycerol with the magnetic volume concentration of 15%. [38]. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

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