A new experimental procedure for characterizing quantum effects in small magnetic particle systems

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Abstract. – A new experimental procedure is discussed, which aims at separating thermal from quantum behavior independently of the energy barrier distribution in small particle systems. Magnetization relaxation data measured between 60 mK and 5 K on a sample of nanoparticles is presented. The comparison between experimental data and numerical calculations shows a clear departure from a standard thermal dynamics scenario, a result which was not obvious without using the new procedure presented here.

The prediction that the magnetic moment of a single domain particle should flip by (quasi-macroscopic) quantum tunneling through the anisotropy barrier has motivated many experiments. Some attempts at a study of a single particle have been made, but most of the experiments have been carried out on a macroscopic number of nanoparticles dispersed in a non magnetic matrix, mainly by measuring the magnetic relaxation after a field change (so-called “viscosity” measurements). In such systems the sizes and the anisotropy constants of the particles are distributed, and an accurate knowledge of these distributions is out of reach, particularly for the very small barriers which are of interest when measuring the slow dynamics at low temperature. In addition, there may exist numerous small energy barriers due to surface defects, making hazardous a simple correlation between the energy barriers and the particle sizes. Consequently, the experimental evidence of quantum tunneling of the magnetization (QTM) based on viscosity measurements in such systems...
remains controversial [7, 8]. In this letter, we present relaxation measurements on small isolated magnetic particles at low temperatures. We describe in the first part the usual analysis of the thermal variation of the magnetic viscosity, emphasizing its limits. In the second part, we discuss a new experimental procedure, which is likely to give much more reliable information on the thermal or quantum nature of the observed phenomena.

Viscosity measurements and their limitations. – The sample consists of small ferrimagnetic particles of $\gamma - Fe_2O_3$ (magnetite) which are dispersed in a silica matrix, with a volume fraction $4 \times 10^{-4}$. A Transmission Electron Microscopy study shows that their sizes can be fitted to a lognormal distribution with peak value $d_0 = 6.3 nm$ and standard deviation $\sigma = 0.25 [9]$. It may thus be considered a good example of isolated single domain particle system. The measurements were taken with a homemade combination of an r.f. SQUID magnetometer and a dilution refrigerator [11]. The sample is coupled to the mixing chamber through a thermal impedance which allows a sample temperature range of 35 mK to 7 K. A 62 Oe magnetic field is applied on the sample at an initial temperature of 6 K, which proved to produce a well defined initial state for subsequent measurements at lower temperatures; as a matter of fact, at 6 K, all the processes that one can measure at lower temperatures are rapidly reaching their equilibrium. This will appear clearly from the simple calculations below, and has been checked by other choices than 6 K [9]. After field cooling the sample down to the desired temperature and waiting for thermal equilibrium(1), the field is cut off and the time change of the magnetic moment is recorded by following the variation of the SQUID signal(2). This method avoids heating problems related to the sample movement at low temperatures, and allows a better sensitivity. We have studied the variation of the moment as a function of the time $t$ after the field cut-off. On one decade of time, between 100 s and 1000 s, the plot is roughly linear in log($t$). Fig.1 shows the average logarithmic slope (viscosity $S$) of $M(t)$ between 100 s and 1000 s for temperatures from 5 K down to 60 mK.

For decreasing temperatures, the measured relaxation rate first decreases, then flattens out and surprisingly increases back below 150 mK. The same result is obtained with a ten times smaller preparation field [9] (the viscosity being proportionally reduced).

For one isolated uniaxial particle of anisotropy barrier $U$, the relaxation time can be written

$$\tau(U, T_0) = \tau_0 \exp \left( \frac{U}{k_B T^*(T_0)} \right)$$

where $\tau_0$ is a microscopic attempt time of the order of $10^{-8}$ s to $10^{-12}$ s. $T^*(T)$ is an effective temperature, which equals $T$ in the case of thermally activated dynamics. The first-order predicted effect of a crossover towards quantum dynamics is that $T^*(T)$ should become greater than $T$ or even temperature independent for temperatures below a certain crossover temperature $T_{ct}$ [4], leading to faster fluctuations than expected from thermal dynamics. Thinking of the sample relaxation at temperature $T_0$ as a sum of independent processes (in our case magnetization reversal of isolated particles), one may write the total magnetic moment $M(t, T_0)$ as

$$M(t, T_0) = \int_0^{+\infty} m_i(U) P(U) \exp \left( -\frac{t}{\tau(U, T_0)} \right) dU$$

(1) By measuring the paramagnetic component of the sample signal [4], we have checked that the sample temperature accurately follows the thermometer temperature in the whole accessible range, with a time constant less than 60 s.

(2) The time spent before the field cut-off has been checked to be of no significant influence on the relaxation rate, in contrast with what has been observed in more concentrated systems, where dipolar interactions may yield aging effects [10].
where \( P(U) \) is the energy barrier distribution, and \( m_i(U) \) is the average initial magnetic moment of the objects of anisotropy barrier \( U \). From eq. (2) and using the usual step function approximation [12], the logarithmic relaxation rate approximates to

\[
S \equiv -\frac{dM(t, T_0)}{d \ln t} \simeq k_B T^* (T_0) P(U_c) m_i(U_c),
\]

where \( U_c \) is the barrier energy of the objects having their main contribution to the dynamics after time \( t \) at temperature \( T_0 \). The distribution \( P(U_c) m_i(U_c) \) has no reason to have a weaker dependence on \( T_0 \) than \( T^*(T_0) \) itself. The crucial point is that the relevant part of this distribution is out of reach in such a system: at low \( T \) and under zero-field, those entities which contribute to the dynamics correspond to very small energy barriers, whose physical origin remains uncertain [4, 6]. Therefore, extracting any \( T^*(T_0) \) (which is the quantity of interest to characterize a departure from thermal dynamics) directly from a measurement of \( S(T) \) is generally not justified, for this implies arbitrary hypotheses over \( P(U) m_i(U) \) [7, 8, 9]. In the next section, we present a new experimental procedure for reliably distinguishing between thermal and quantum dynamics, a procedure which is almost insensitive to the distribution \( P(U) m_i(U) \).

Disentangling thermal from quantum dynamics. – The point is that the temperature dependence of the relaxation rate is much weaker in the quantum regime than in the thermal regime. Hence the following idea: the thermal part of the relaxation towards equilibrium should rapidly be exhausted by a pre-relaxation at a higher temperature, which in contrast should be of little influence on quantum processes. Such a procedure is sketched in fig. 2a.

After field cooling the sample from 6 K to a temperature \( x.T_0 \) higher than \( T_0 \), we cut off the field, wait for \( t_0 = 200 \) s and then cool down the sample to \( T_0 \). Still considering independent relaxation processes, and neglecting as a first approximation a possible \( x \)-dependence of the initial moments, we write the relaxation of the total magnetic moment as

\[
M(t, T_0, x) = \int_0^{\infty} P(U) m_i(U) \exp\left(-\frac{t_0}{\tau(U, x.T_0)}\right) \exp\left(-\frac{t - t_0}{\tau(U, T_0)}\right) dU.
\]
As a first step, we now give a qualitative interpretation of our procedure, using the same kind of approximation as in eq. 3. The logarithmic slope \( S(T_0, x) \) of \( M \) around time 1000 s after the field cut-off roughly corresponds to the product of the standard \( S(T_0) \) with a damping factor due to the pre-relaxation at \( x = T_0 \). By dividing \( S(T_0, x) \) by \( S(T_0) \), \( P(U_c) m_i(U_c) \) is eliminated (see eq. 3), and we obtain a quantity which we may call “residual memory ratio” (RMR), in the sense that it represents the memory of the initial state that the system has kept through the whole procedure.

Beyond this only qualitative argument, we have performed a complete calculation of eq. 4, and checked that the variation of this ratio \( RMR(x) = S(T_0, x)/S(T_0) \) indeed contains a very strong information upon \( T^*(T) \), while being remarkably insensitive to the \( P(U_c) m_i(U) \) distribution. We have calculated the time variation of \( M \) and its average logarithmic slope between log\( (t) = 3.0 \) and log\( (t) = 3.2 \) (this choice has been checked to be of no influence and is related to the experimental procedure described below). In fig. 2b is plotted the calculated \( RMR(x) \) for various hypotheses on \( T^*(T) \) and \( P(U) m_i(U) \), with \( \tau_0 = 10^{-10} \) s.

In the thermal case (fig. 2b curves (i)), \( RMR(x) \) is the same for all working temperatures \( T_0 \); in a plateau hypothesis for quantum dynamics (fig. 2b curves (ii)), \( RMR(x) \) shows a corresponding plateau, followed by a sharp decrease at \( x = T_{cr}/T_0 \). An insert shows \( T^*(T) \) in each case. Three choices of \( P(U) m_i(U) \) are presented.

In both cases, the curves are very weakly dependent on the \( \tau_0 \) value; for instance, in the thermal case, we have computed that the \( x \)-value at which \( RMR(x) \) has decreased by 90% ranges from 1.15 for \( \tau_0 = 10^{-8} \) s to 1.20 for \( \tau_0 = 10^{-12} \) s.

A crucial result is that, as is clear from fig. 2b, the calculated \( RMR(x) \) is nearly insensitive to the extremely broad choice of \( P(U) m_i(U) \) presented here (ranging from \( U^{-5} \) to \( U^{+5} \)), while it clearly reflects the thermal or quantum nature of the dynamics. Thus, within our present description, thermal dynamics can be characterized by a sharp decrease of RMR at low \( x \). We have assumed temperature independent barriers \( U \); in that respect, interactions between the...
particles must be negligible. This was our motivation for choosing a sample of highly diluted particles. Also, we do not consider the case of a singular $P(U) m_i(U)$; for instance, in the case of a delta-function peaking at $U \gg U_c$ (see eq.3), the thermal $RMR(x)$ would exhibit a slower $x$-decrease, but this would imply a very sharp temperature dependence of the viscosity, in disagreement with our present result.

We have applied the procedure sketched in fig.2a to measurements on the same sample as in fig.1; the results are shown in fig.3a.

![Figure 3a](image1.png) ![Figure 3b](image2.png)

**Fig. 3.** a) Measured $RMR(x)$ from 3 $K$ down to 60 $mK$ (symbols). The solid line is the calculation for thermally activated dynamics (see fig.2b (i)). b) Calculated $RMR(x)$ for the $T^*(T)$ shown in the insert, for different choices of $T_0$.

For $T_0 = 3$ $K$ and $T_0 = 2$ $K$, $RMR(x)$ is very close to what is expected in the thermal regime. For lower temperatures, the observed $RMR(x)$ can no more be explained in terms of thermal dynamics: its variation with $x$ becomes slower and slower as temperature decreases, in an intermediate fashion between the two extreme cases plotted in fig.2b. The behavior clearly departs from the thermal case of fig.2b(i); however, when compared with the ideal plateau case of fig.2b(ii), the smooth decrease of $RMR(x)$ is suggestive of a distribution of crossover temperatures $T_{cr}$ in the system, or of a possible influence of an $x$-dependence of the initial moments.

Keeping the same hypotheses as for eq.4, we have computed $RMR(x)$ for a simplistic $T^*(T)$ shape as displayed in fig.3b. We have chosen this $T^*(T)$ shape in order to obtain a qualitative agreement with our present experimental data. This $T^*(T)$ would still be of about 0.5 $K$ at our lowest measurement temperature (0.06 $K$): this is far beyond any experimental uncertainty on the temperature of our sample. The $T^*(T)$ shape, together with the measured $S(T)$ variation of fig.1, yields through eq.3 an estimate of the distribution $P(U) m_i(U)$. It increases towards small energy barriers, as suggested but not proven in [9]. This calls for a better knowledge of the physical origin of low energy barriers in such samples.

As a conclusion, this new procedure brings significant information on the nature of the dynamics, almost independently of the magnetic moment distribution $P(U) m_i(U)$. The method has
allowed us to evidence a significant departure from the expected thermal dynamics scenario in an assembly of small magnetic particles. In our opinion, this method should help evidencing and studying QTM in many-particle samples, and could be interestingly extended to the characterization of non-thermal behavior in other systems, such as depinning of vortices in superconductors or of Bloch walls in ferromagnets.

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