Magnetization dynamics of single-domain particles by superparamagnetic theory

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Abstract

The state of the art in the theory of dynamic response properties of single-domain particles (macropins) is presented. If allowing for thermofluctuational effects, one admits temperature as an essential parameter. This implies substantial modification of classical results of magnetodynamic phenomenology from quasi-static hysteresis of magnetization to FMR. With a number of examples we demonstrate how this work is done on the basis of Brown’s kinetic equation.

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1. Introduction

Magnetodynamics of nanoparticles has, for decades, been the focus of fundamental and applicational research. The main objective, driven by the needs of information storage and recording is to find a way for manufacturing nanoparticle assemblies satisfying a set of stringent requirements. Among them: (i) to be dense but retain individuality of each particle, (ii) to be easily remagnetizable but, if not excited, keep the magnetic state for a considerable time, (iii) to be simple in synthesis but be monodisperse as perfectly as possible. The essential question that technologists and engineers address to the fundamental science is under what conditions the self-contradicting requirements become self-exclusive ones. To a good part, this problem focuses on superparamagnetism (SP). From this viewpoint, the work being done on this subject is in pursuit of an answer to the afore-posed question of finding the limit and investigation of what is possible before one hits it.

Experimentally, the insight to individual particle behavior has been advanced greatly by micro-SQUID measurements on isolated nanograins [1]. For the studies of the assembly behavior, magnetic fluids, initially invented for completely different purposes, are now very helpful. These media are very convenient since they easily facilitate a change interparticle distances (by dissolving) and tuning of the distribution of the particle easy axes (by preparing FC and ZFC samples), see Ref. [2].

In our opinion, phenomenological magnetodynamics is an efficient approach to the problem. Dealing for some time with simple analytical models, see review articles [3–5], we are convinced in their ability to account for basic facts. Hereby we focus on the development of SP theory referring to some essential particular results.

2. Fundamentals

As a comprehensive starting point let us take the commonly known Néel formula \( \tau_N = \tau_0 e^{E_A/kT} \), where \( \tau_0 \) is the attempt time and \( E_A \) determines the anisotropy term in the orientation-dependent magnetic energy of a single-domain particle:

\[
U = -\mu(eH) - E_A(e\cdot n)^2, \quad \mu = \mu e, \quad |e| = 1,
\]

where \( \mu \) is the magnetic moment and \( n \) the easy axis direction. By definition, \( \tau_N \) characterizes the rate of spontaneous inversions of the particle magnetic moment.
at $H = 0$ in the temperature range $\sigma = E_A/kT > 1$. In this random process vector $e$ surmounts the potential barrier separating two equal energy minima in the orientational space, so $\tau_N$ is often called the interwell time. Accordingly, the response time of $e$ within the same energy minimum is called the intrawell time, it is of the order of $\tau_0$.

In its original form, $\tau_N$ is valid only for the case of zero external field and relatively high barriers $E_A$. A correct way to obtain the interwell time for arbitrary constant fields and barriers was shown by Brown [6] who introduced a concept of magnetic moment orientational thermal diffusion and derived the corresponding Langevin and Fokker–Planck (FP) equations. In this scope, the underlying dynamic equation is taken from phenomenology in either Gilbert or Landau–Lifshitz forms. Choosing the latter, one has

$$\frac{d}{dt}e = -\gamma(e \times H_{\text{eff}}) - \alpha e + (e \times (e \times H_{\text{eff}})),$$

where $\gamma$ is the gyromagnetic ratio and $\alpha$ the precession damping parameter; the effective internal field is defined by $H_{\text{eff}} = -(1/\mu)\partial U/\partial e$. The Brown kinetic equation describes the evolution of the probability density function $W(e, t)$:

$$2\tau_D \partial W/\partial t = JWJ(U/kT + \ln W),$$

where $\tau_D = \tau_0\sigma$ is the reference time of orientational diffusion of $e$ inside the particle body and $J = (e \times \partial/\partial e)$ infinitesimal rotation operator.

Under stationary conditions and $H = 0$, Eq. (3) produces a set of eigenvalues $\lambda_i$ where the first one differs from all the other by its exponential behavior $\lambda_1 \propto \exp(-\sigma)$ for $\sigma \gg 1$. All the decrements with $i \geq 2$ are of the order of $1/\tau_D$ and thus but weakly depend on temperature. Although $1/\lambda_1$ intuitively is often associated with Néel time, this resemblance is limited even at $H = 0$. For one thing, at $\sigma < 1$ the time $\tau$ must tend to $\tau_D$. Yet more important is the fact that at any non-zero $\sigma$ the set of eigenfunctions $\{\Psi_i\}$ of Eq. (3) does not coincide with Legendre polynomials of the coordinate angles of $e$. Thence, the observed magnetic moment (its projection $\mu \cos \theta$ on the easy axis) gets contributions from all $\Psi_i$, each evolving with its own $\lambda_i$. The net result for relaxation of vector $e$ is given by the so-called integral time $\tau_{\text{int}}$. At low temperatures a major contribution to $\tau_{\text{int}}$ is due to the decrement $\lambda_1$ which can be derived in the form of asymptotic series in $1/\sigma$ [7]. For the case $H \neq 0$ an asymptotic formula valid for $h = \mu H/2E_A < 1$ was given by Aharoni [8]. Unlike $1/\lambda_1$, which even in principle cannot be evaluated analytically for arbitrary $\sigma$ and $h$, an exact expression for $\tau_{\text{int}}(\sigma, h)$ is available [9]. This formula may be written in a finite form in terms of hypergeometric (Kummer’s) functions. In Ref. [10] a compact numeric representation for $\tau_{\text{int}}$ at arbitrary $\sigma$ and $h$ is constructed.

3. Low-frequency range

The set of temperature-dependent intrawell and interwell times determines the low-frequency magnetodynamics of nanoparticles. The appropriate theory in the linear response approximation is easy to build, the emerging dynamic susceptibilities are directly connected to the relaxational spectrum of the system. However, when applied to experiment, this approach inherently retains a wide margin for uncertainty in estimating phenomenological material parameters like $\tau_0$, $\mu$, etc. Extending the theory by including nonlinear responses, provides additional relationships and thus helps to clarify the situation. In Ref. [11] an example is given to the effect that taking into account together the linear and cubic susceptibilities ensures adequate understanding of the low-frequency magnetic spectroscopy data on Cu–Co nanoprecipitates.

Besides ordinary weak AC field probing, the SP theory gives a direct way to explain and analyze the details of the magnetic stochastic resonance. As a noise-driven bistable system, a nanoparticle differs essentially from a model one-dimensional oscillator. Its specifics is due to two major facts: (i) the response is always a “mixture” of intrawell and interwell relaxations and (ii) as soon as the applied AC field is tilted with respect to the particle easy axis, the noise-driven oscillations due to gyromagnetism become two-dimensional. In SP framework all this is accounted for in a natural way [12]. As well, it gives a clear and consistent description of the effect in the situation where a constant bias field, making the wells non-equal, is imposed [10]. For this case SP theory yields quite an unexpected prediction: the stochastic resonance peak becomes yet more pronounced when the AC field polarization tends to point normally to the easy axis [13]. Fig. 1 illustrates this.

Yet more interesting appears the case of cubic bulk anisotropy where the easy axes are multiple. Here the magnetizing field is always non-parallel to some of them, and in SP problem the longitudinal (low-frequency) and precessional (high-frequency) modes of the magnetic

Fig. 1. Signal-to-noise ratio of a uniaxial nanoparticle in the probing field making angle $\beta$ with the easy axis; the lower dashed line is $\beta = 0$. 
moment are strongly coupled yielding a non-trivial dependence of the signal-to-noise ratio on the precession damping parameter $\alpha$ [14].

SP theory accounting for strong nonlinearities, i.e., forced re-magnetizing, is necessary if one wants to describe dynamic hysteresis in nanoparticles including low-temperature regimes where the loop has to approach the Stoner–Wohlfarth shape. Here one deals with the problem where the magnetic relaxation time $\tau(\sigma, h)$ is modified “on the flight” changing periodically from a very long ($\sim \tau_s$) to a very short one ($\sim \tau_D / h$). The squareness of the emerging loop depends on the relation of the rate of the field sweep and the value of the magnetic response time. For the case of the field applied along the easy axis, where the limiting Stoner–Wohlfarth contour is a rectangular, the pertinent study is carried out in Refs. [15,16], the sequence of loops is shown in Fig. 2. As expected, SP treatment enables to obtain the dependencies of the loop area $A$ (absorption) on the main governing parameters, viz. temperature, field amplitude, and field frequency, an example is given in Fig. 3. These dependencies may be immediately compared to the conventionally adopted scaling $A \propto H^3 \omega^\beta T^{-\gamma}$, see Ref. [17], for example. As none of the obtained SP functions does change as a power law, in this context the ubiquitous difficulties with non-constancy of the indexes encountered in experiment seem but natural.

4. High-frequency range

4.1. Non-zero external field

The magnetodynamic equation (2) is in common use due to its ability to give a reliable description of ferromagnetic resonance (FMR). The reference frequency of the magnetic moment precession is of the order $\gamma H_{\text{eff}}$ and belongs to ultra-high range. To account for superparamagnetic effects in FMR, Brown kinetic equation is modified [18] by introducing there the precession term

$$2 \tau_D \partial W / \partial t = JW(J + x^{-1}(\partial / \partial a))(U/kT + \ln W).$$

With Eq. (4) for each classical FMR problem its SP extension may be built. The linear dynamic susceptibility $\chi(\omega)$ of an isotropic ($E_A = 0$) nanoparticle is the most easy to get and analyze [19]. The theory predicts that the precession frequency, as a parameter in $\chi(\omega)$, does not change with temperature. Meanwhile, the damping parameter is renormalized as

$$\alpha_c = [1/L(\xi_0) - 1/\xi_0], \quad \xi_0 = \mu H_0 / kT,$$

where $H_0$ is the magnetizing field and $L$ the Langevin function. This result means monotonic broadening of the absorption line $\chi' \omega$ with temperature. Surprisingly, it contradicts direct experimental observations where typically the peak-to-peak width of the absorption line of a nanosystem under temperature increase becomes narrower (Fig. 3).

Of course, in real materials the general tendency imposed by thermal fluctuations might be well masked by temperature dependencies of magnetic material parameters. However, as had been shown in Ref. [20], SP model can acquire the said temperature behavior if to add to a particle some bulk anisotropy $\sigma < \xi_0$. Then at low temperatures ($\sigma, \xi_0 > 1$) in a randomly oriented assembly of uniaxial nanoparticles the resonance conditions for different magnetic moments are different. Due to this non-uniform broadening the linewidth $\Delta H$ is as large as $\sim (3\sigma / \xi_0)H_0$. With temperature growth the ratio $\sigma / \xi_0$ does not change but the system is driven to the state where yet $\xi_0 < 1$ but $\sigma$ goes below unity. The latter entails effective “melting down” of the anisotropy field so that the resonance condition tends to universal expression $\omega_{\text{res}} = \gamma H_0$. Accordingly, the linewidth decreases gradually to the value $\sim 2H_0$. Only after the system is heated yet further, up to $\xi_0 \approx 1$, the broadening mechanism of Eq. (5) takes over. The two mentioned limiting behaviors of $\Delta H$ may be found

![Fig. 2. Dynamic hysteresis: normalized average magnetization $\langle \cos \theta \rangle$ at the field frequency $\omega \tau_s = 10^{-2}$ for anisotropy parameter $\sigma = 4$ (short dashes), 16 (solid), $\infty$, i.e., Stoner–Wohlfarth (long dashes).](image)

![Fig. 3. Dynamic hysteresis: normalized loop area $A/h$ as a function of frequency $\omega \tau$ and field amplitude $h$ for dimensionless temperature $\sigma = 10$.](image)
analytically; they are [20]:
\[
\frac{\Delta^{(1)} H}{H_0} = \frac{2\omega}{\sqrt{3} \xi_0 L}, \quad \frac{\Delta^{(2)} H}{H_0} = 3\sigma \xi_0 - 3L,
\]
and are shown in Fig. 4 by dashed lines. With their help, the net curve \(\Delta H(\xi_0)\) is easy to understand: at the right end \(\Delta H\) diminishes with temperature (non-uniform broadening “melts down”) while at the left end \(\Delta H\) begins its formally unlimited increase due to growth of thermal fluctuations.

4.2. Zero external field. Intrinsic FMR

In SP theory the situation where precession takes place exclusively in the internal anisotropy field, i.e., at \(H_0 = 0\), is the most interesting one. In this case the Landau–Lifshitz equation for a uniaxial particle takes the form
\[
\frac{d}{dt} e = -\omega_A(e\times n) + \alpha(e\times (e\times n))
\]
with \(\omega_A = 2\gamma E_A/\mu\). Let us remark on two essential points. First, Eq. (7) is even with respect to the axis \(n\) that means that, unlike the case \(H_0 \neq 0\), this system has the same response to probing fields with clockwise and anti-clockwise polarizations. Second, the precession frequency, which from Eq. (7) may be effectively written as \(\omega_A \cos \delta\), depends strongly on the angle that the magnetic moment makes with the easy axis and even tends to zero for \(\delta = 0\).

Normally, in linear response treatment this “angular modulation” is ignored. SP theory imparts a precise meaning to this assumption: it holds not longer than condition \(\sigma \gg 1\) is valid, that is for large enough particles and/or low enough temperatures. In a SP particle assembly with \(\sigma \sim 1\) the resonance frequencies are “smeared” over the interval \([0, \omega_A]\), and this circumstance changes drastically the linear susceptibility. As first pointed out in Ref. [21] even for a single particle the line must be constructed as a result of a specific non-uniform broadening. A consistent SP calculation is given in Ref. [22] based on Kubo theorem. The result is remarkable: in the \(z = 0\) limit, i.e., in the case where the line is formed exclusively by thermal spread of the particle eigenfrequencies, the absorption line (normalized for a particle) is
\[
\chi' = \frac{\mu^2}{E_A \omega_A} \frac{\sigma \omega}{\omega_A} \left[ 1 - \left( \frac{\omega}{\omega_A} \right)^2 \right] \exp\left( \frac{\sigma \omega^2}{\omega_A^2} \right),
\]
where function \(R_\sigma\) for \(\sigma \lesssim 1\) is of the order of unity. Note that in intrinsic FMR the sweeping parameter is the probing field frequency \(\omega\).

Eq. (8) has a striking resemblance with the so-called Landau damping lineshape, first introduced in the theory of ionized plasma. The underlying idea, however, is that this type of line always emerges in cases where a Lorentz line is averaged over a Boltzmann equilibrium distribution of eigenfrequencies. However, the intrinsic FMR in a single particle is specific by the fact that here the line comes out as if the Boltzmann factor were inverted: note that the argument of the exponential is positive. This happens because, unlike translational degrees of freedom, the meridional coordinate of the magnetic moment is confined to the interval \(0 \leq \theta \leq \pi\). The dynamic susceptibility in the form (8) has a single absorption peak whose width has a remarkable temperature behavior illustrated in Fig. 5. It turns out that if the precession quality factor is high (low damping) the ultimate heating-induced broadening of the absorption line is “postponed”. Meanwhile, the linewidth acquires intermediate asymptotic behavior \(\Delta \omega = \text{const}(T)\), which is not at all intuitively expectable given the monotonic growth of intensity of fluctuations with temperature.

Specific behavior entailed by long-living \((z \ll 1)\) precession of the magnetic moment in the absence of imposed field causes an interesting nonlinear effect predicted in Ref. [23]. Namely, in an AC field \(H\) of frequency \(\omega\) tilted at some angle with respect to the particle easy axis, the cubic susceptibility \(\chi^{(3)}\), i.e., the part of the projection \((\mu)\) that is proportional to \(H^3\) is considered. In the vicinity of \(\omega \sim 1\) (intrawell dispersion) it displays relaxation maxima whose absolute values are the greater the smaller the precession damping parameter \(z\). The enhancement found occurs due
to the fact that the probability of an interwell transition is higher the longer the magnetic moment stays at the outer orbit and passes close to a temporal saddle point created by a tilted AC field at the otherwise axially symmetrical potential barrier. For general discussion of the coupling between relaxational and precessional modes at arbitrary $\alpha$, see Ref. [24].

Only recently the essential role of finite-size effects and surface properties for the net magnetodynamics of nanoparticles was realized [25,26]. In phenomenology, OSP theory is modified by passing from $K V$ to $(K_u + K_s/d)V$ in the representation of uniaxial anisotropy, where $V$ is the volume and $d$ the diameter of the particle. Whatever simple, it proved to be quite good in reflecting “imprinted” and field-tuned (exchange bias) contributions to FMR. To distinguish between those, field-frozen and zero-field frozen samples of magnetic fluids are very useful, see Ref. [26, Chapter 5]. Moreover, in the particle size range $<10$ nm the surface term appears to dominate completely. Besides that, the size dependence $\propto d^2$ of the surface term strongly affects all the polydispersity averages. Intrinsic FMR provides a clear example of that. Indeed, in the $\alpha \to 0$ limit the reference frequency for a particle with bulk anisotropy $\omega_A = 2 K_v V/\mu$ does not depend on the particle size. However, when the surface contribution dominates it becomes $\omega_A = 2 K_s V/\mu d$. Thence, averaging over a histogram becomes dependent on the value of $d$ and its distribution width; in Ref. [27] it is shown to be a strong effect.

5. Conclusion

Magnetodynamics of nanocomposites, being a complex combination of individual and collective properties, implies a great variety of behavior of those systems. Much of this variety is predetermined by the magnetodynamic response of individual particles. Phenomenological SP theory, as we show here, is quite good in revealing the essential physics of the latter. Not at all pretending to be an exhaustive description, it makes an efficient tool in both planning numeric simulations and understanding their results.

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