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The effect of the external magnetic field on the thermal relaxation of magnetization in systems of aligned nanoparticles

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Abstract

The dynamics of magnetic relaxation in a system of isolated ferrimagnetic nanoparticles depends on the ratio between the magnetic relaxation time (τ) and the measurement time (t_m), which is usually considered to be equal to the period (T_H) of the external alternating magnetic field ($t_m = T_H$). When t_m approaches τ ($\tau < t_m$), the magnetic moments cannot relax completely, thus leading to a deviation from the superparamagnetic behaviour (SPM), and a magnetic remanence of the system when the deviation is large. An external magnetic field (H) can significantly change the dynamics of the relaxation, especially when its amplitude (H_m) is high. This paper shows that there is a limit field (threshold field (H_p)) that depends on the anisotropy field of the nanoparticle, its magnetic volume and on the temperature; beyond this field, the magnetic moments cannot pass the potential barrier and they remain blocked. It will be shown that under these conditions the measurement time can no longer be considered to be $t_m = T_H$, but is a measurement time $t_{mH} < T_H$ that in addition to T_H will also depend on H_p and H_m . When the amplitude of the alternating magnetic field is lower than the value of the threshold field ($H_m < H_p$), the measurement time is reduced to the period of the magnetic field. The theory proposed for a system of aligned nanoparticles has been verified experimentally in the case of a ferrofluid-type system. The result obtained brings in important corrections for determining the magnetic volume of the nanoparticles or the magnetic anisotropy constant if the condition $t_m = t_{mH} < T_H$ is used when H_m is high ($H_m > H_p$), instead of $t_m = T_H$.

1. Introduction

Multifunctional magnetic nanoparticles are gaining more interest in theoretical and experimental studies [1–3] as a result of their potential applications, such as in ultrahigh density

recording media and biomedicine [4–7], since they can easily be manipulated and controlled with an external magnetic field. Applications regarding information storage and recording media are primarily based on the high values of the coercivity of a single-domain nanoparticle at an alternating magnetization along the direction of which its magnetic moment is oriented when the magnetization is thermally stable. However, the stability at a given temperature will also depend on the value of the energy barrier for the magnetic moments (W_b), which, in its turn, in the absence of other external factors will depend on the nanoparticle's volume for a certain material. Thus, depending on the nanoparticle's volume there will be a lower limit of the magnetization stability corresponding to a critical volume [8]; below the critical volume there will be fluctuations of the nanoparticle's magnetization under the effect of the thermal activation.

In practical applications, an external magnetic field is applied to the nanoparticle system in most cases. Under these conditions the energy barrier changes under the effect of the external magnetic field; hence it is important to know its effect on the magnetic relaxation. Below the critical volume, after applying an external magnetic field for saturation, the magnetic moments will rotate in the direction and in the sense of the applied field, resulting in a saturation magnetization. After removing the field, $n/2$ magnetic moments out of the total n will invert during the relaxation time [9, 10]

$$\tau_N = \tau_0 \exp\left(\frac{W_b}{k_B T}\right), \quad (1)$$

and the system's magnetization $M_r(t) = M_{\text{sat}}(0) \cdot e^{-t/\tau_N}$ decreases during the time τ_N to the value e^{-1} ($\sim 37\%$) of the saturation value $M_{\text{sat}}(0)$ (at the initial moment $t = 0$). The barrier energy (W_b) in this case (in the absence of the external magnetic field) is given only by the magnetic anisotropy energy, $W_b = K_a V_m$, K_a being an effective anisotropy constant and V_m the magnetic volume of the nanoparticle. Other values in equation (1) are: T the temperature, k_B Boltzmann's constant and τ_0 a time constant which is usually 10^{-9} s. In usual ferrofluids, the main relaxation mechanisms of magnetization are either of Néel type (relaxation of magnetization by the rotation of the magnetic moment in relation to the crystallographic axes) or of Brown (Debye) type (relaxation of magnetization by the rotation of the magnetic moment together with the particle itself). In the presence of thermal agitation ($T > 0$) and in the absence of the external magnetic field, or when the field is present but the condition $\xi \ll 1$ is met ($\xi = \mu_0 m_p H / k_B T$, where ξ is the ratio between the energy of the magnetic moment for particle m_p in the field H and the thermal energy $k_B T$ ($\mu_0 = 4\pi \times 10^{-7} \text{ H m}^{-1}$)), the relaxation times corresponding to the two processes can be described by the equations

$$\tau_N = \tau_0 \exp(K_a V_m / k_B T), \quad (2)$$

where τ_N is the Néel relaxation time [9], and

$$\tau_B = 3\eta V / k_B T, \quad (3)$$

where τ_B is the Brown relaxation time [10]. In equation (3), η is the viscosity of the carrier liquid and V is the hydrodynamic volume. Normally, for most ferrofluids, at room temperature $\tau_N \ll \tau_B$. However, depending mainly on the particle's anisotropy and volume, but also on the values of η and T , there can be cases when the two relaxation times become comparable. In this case, the relaxation time (τ) of magnetization is well described by the equation [11]

$$\tau = \tau_N \tau_B / (\tau_N + \tau_B). \quad (4)$$

Moreover, in the case of strong fields ($\xi \gg 1$), the relaxation time of the particle orientation (τ_n) depends on the ratio between the external field H and the field of the particle's magnetic

anisotropy H_K ($H_K = 2K_a/\mu_0M_s$, M_s is the spontaneous magnetization) [12]; this means that for $H/H_K \ll 1$, τ_n is defined by the equation

$$\tau_n = 6\eta V/(\mu_0M_s H V_m) \quad (5)$$

and for $H/H_K \gg 1$,

$$\tau'_n = 3\eta V/(K_a V_m). \quad (6)$$

In the presence of the external magnetic field H , the barrier energy of the nanoparticle will change (either increase or decrease),

$$W_b = W_{\max} - (\pm W_{\min}), \quad (7)$$

depending on the orientation of the field, in the sense of the nanoparticle's magnetic moment or in the opposite sense. In equation (7), W_{\max} is the maximum energy and W_{\min} is the minimum energy of the nanoparticle in the field. At the same time, the barrier energy depends on the orientation of the easy magnetization axes of the nanoparticles, regardless of whether these are aligned or not (in the direction of the magnetic field or in any other direction), which will have a direct influence on the magnetic relaxation.

Under dynamic conditions, the stability of magnetic moments can be analysed as depending on the ratio between the measurement time (t_m ; the time during which the magnetic relaxation process is being observed) and the magnetic relaxation time τ . Statically, the measurement time is $10\text{--}10^2$ s. Dynamically, however, it will depend on the period (T_H) of the magnetizing field and usually it is assumed to be [13, 14]

$$t_m = T_H. \quad (8)$$

This equation only applies in the presence of thermal agitation and only for very low amplitudes of the external magnetic field (generally of the order of Oe) [14, 15]. When the amplitude of the field is no longer small, equation (8) does not apply any longer. Under these conditions, the equation must be corrected. This aspect can already be observed very well from the experimental results, when the variation of the initial magnetic susceptibility in relation to temperature is recorded for a nanoparticle system [16]; if the magnetic field where the susceptibility was recorded is low (a few Oe) and in the absence of other external factors and interactions, a maximum susceptibility is obtained at the blocking temperature (when the measurement time becomes equal to the mean relaxation time ($t_m = \tau$)) [14, 15]. When the magnetic field is higher (tens of Oe or even more), the maximum susceptibility no longer corresponds to the previous position (on the temperature scale) and it is shifted for other values of the temperature [16–18]; the extent of shifting depends on the value of the magnetic field. As a result, when equation (8) is used in this case there will be significant errors, for instance when the magnetic anisotropy constant (K_a) or the volume of nanoparticles ($\langle V_m \rangle$) is being determined,

$$K_a \langle V_m \rangle = \langle T_b \rangle \cdot k_B \ln\left(\frac{T_H}{\tau_0}\right), \quad (9)$$

from the blocking temperature $\langle T_b \rangle$ (considered as being the temperature that corresponds to the maximum of magnetic susceptibility; $\langle \rangle$ is the mean value) determined experimentally, a case that often arises in practice.

In this paper we will present a study on the influence of the high external alternating (harmonic) magnetic field on the magnetic relaxation under dynamic conditions in the case of a system of aligned nanoparticles. In this case we will deduce the mathematical expression for the measurement time (t_{mH}) and we will show that, at a given period of the magnetic field, it depends both on the amplitude of the external magnetic field and on a threshold field, specific

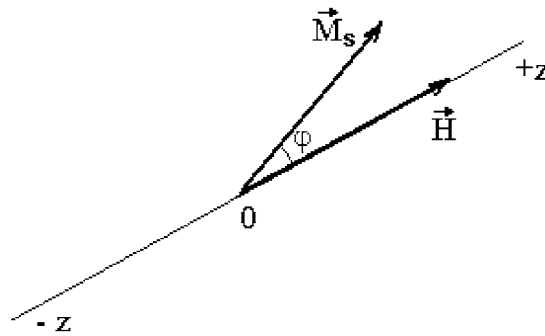


Figure 1. Orientation of the vectors \vec{M}_s and \vec{H} in relation to the easy magnetization axis ($-z, +z$); φ is the angle between the direction of the magnetization and that of the magnetic field.

to the nanoparticle type (depending on the nature of the nanoparticle, at a given temperature and volume). The theoretical results obtained will then be compared to the experimental data and, based on that, the recorded remanence is explained at the temperature of liquid nitrogen for a system of aligned nanoparticles dispersed in a carrier liquid (ferrofluid), a system that has a superparamagnetic behaviour at room temperature.

2. Theory

In the absence of thermal agitation ($T = 0$), the relaxation time according to equation (1) becomes infinite. The energy of a nanoparticle fixed in space, with the magnetic moment $\vec{m}_p = V_m \vec{M}_s$ in the field \vec{H} , the direction of which is the same as that of the easy magnetization axes of the nanoparticle (figure 1), is [19]

$$W(H, \varphi) = K_a V_m \sin^2 \varphi - \mu_0 H M_s V_m \cos \varphi, \quad (10)$$

whereby φ is the angle between the direction of the spontaneous magnetization and that of the easy magnetization axis (the magnetic field is in this direction). In equation (10), the first member is the anisotropy energy (considered as being uniaxial), and the second member is the magnetic moment energy in the field H . From the extreme condition of the energy

$$(dW(H, \varphi)/d\varphi)|_H = 0, \quad (11)$$

it results that

$$(2K_a \cos \varphi + \mu_0 H M_s) \cdot \sin \varphi = 0. \quad (12)$$

The condition $\sin \varphi = 0$ leads to a minimum of the nanoparticle's energy, namely

$$W_{\min} = -\mu_0 H M_s V_m \quad (13)$$

for $\varphi = 0$ (\vec{M}_s and \vec{H} have the same direction and the same sense) and

$$W'_{\min} = +\mu_0 H M_s V_m \quad (14)$$

when $\varphi = \pi$ (\vec{M}_s and \vec{H} have the same direction, but opposite senses). The maximum condition for the energy results from the equation

$$2K_a \cos \varphi + \mu_0 H M_s = 0, \quad (15)$$

which leads to

$$\cos \varphi = -\frac{\mu_0 M_s H}{2K_a}. \quad (16)$$

If, we replace $\cos \varphi$ in equation (10), we obtain the maximum value of the nanoparticle's energy in the presence of the field H :

$$W_{\max} = \frac{\pi K_a d_m^3}{6} \left[1 + \left(\frac{\mu_0 M_s H}{2K_a} \right)^2 \right]. \quad (17)$$

In equation (17) we have used $V_m = \pi d_m^3/6$ (in the approximation of spherical particles), where d_m is the magnetic diameter of the nanoparticle. When the field H increases, according to equation (7), the height of the energy barrier $W_b = W_{\max} - W_{\min}$ increases ($W_{\max} + \mu_0 H M_s V_m$) for nanoparticles that have their magnetic moments oriented in the sense of the applied magnetic field. For the nanoparticles that have their magnetic moments oriented in the opposite sense to the external magnetic field, the energy barrier will decrease ($W_{\max} - \mu_0 H M_s V_m$).

When the magnetic field H decreases after it has reached the saturation value, as long as the height of the energy barrier remains considerable for the magnetic moments, these will not be able to pass the energy barrier and they will retain their orientation (in the sense of the magnetic field). Still, the magnetic moments will only be able to pass the energy barrier when the external field decreases below a certain value, and we will call this field a 'threshold' field (H_p). We will deduce the mathematical expression for the threshold field in the following.

In the presence of thermal agitation, the probability [20]

$$P = P_0 \exp\left(-\frac{W_{\max} - W_{\min}}{k_B T}\right) \quad (18)$$

that the magnetic moment of the nanoparticle will pass the energy barrier in the presence of the field H is

$$P = P_0 \exp\left[-\frac{\pi K_a d_m^3}{6k_B T} \left(1 + \frac{\mu_0 M_s H}{2K_a}\right)^2\right] \quad (19)$$

where P_0 is a factor that varies slightly with the field [21]. In equation (18) we have replaced W_{\max} given by equation (17) and W_{\min} given by equation (13). In this case, the behaviour of the relaxation will be determined by the exponential function (P_{\exp} ; figure 2(a)). Thus, the height of the energy barrier

$$W_b = K_a V_m + \mu_0 M_s V_m H + \frac{\mu_0^2 M_s^2 V_m}{4K_a} H^2, \quad (20)$$

is higher than $K_a V_m$ and its value depends strongly on the value of H .

In the case when the magnetic field has a sinusoidal variation and a high amplitude (the amplitude of the magnetic field (H_m) is higher than the value of the threshold field (H_p ; $H_m > H_p$))—a case often seen in practice—the inversion of magnetic moments can only occur during a short period of time (Δt), in the proximity of the moment when the field will pass the zero value (figure 2(b)). In this case, this time period can be considered to be the *measurement time* (t_{mH} ; period of time during which the magnetic relaxation occurs) of remanence ($\Delta t \equiv t_{mH}$). Figure 2(a) also shows the variation of the magnetic field during a half-period ($T_H/2$). Since the probability is an exponential function, the time t_{mH} can be determined from the practical condition for the decrease of probability (after t_{mH}) at a value of $1/e$ (e—base of the natural logarithm) from the maximum value (P_M ; figure 2(a)). Hence, imposing the condition

$$P = P_M/e, \quad (21)$$

where, in agreement with equation (19),

$$P_M = P_0 \exp\left(-\frac{\pi K_a d_m^3}{6k_B T}\right) \quad (22)$$

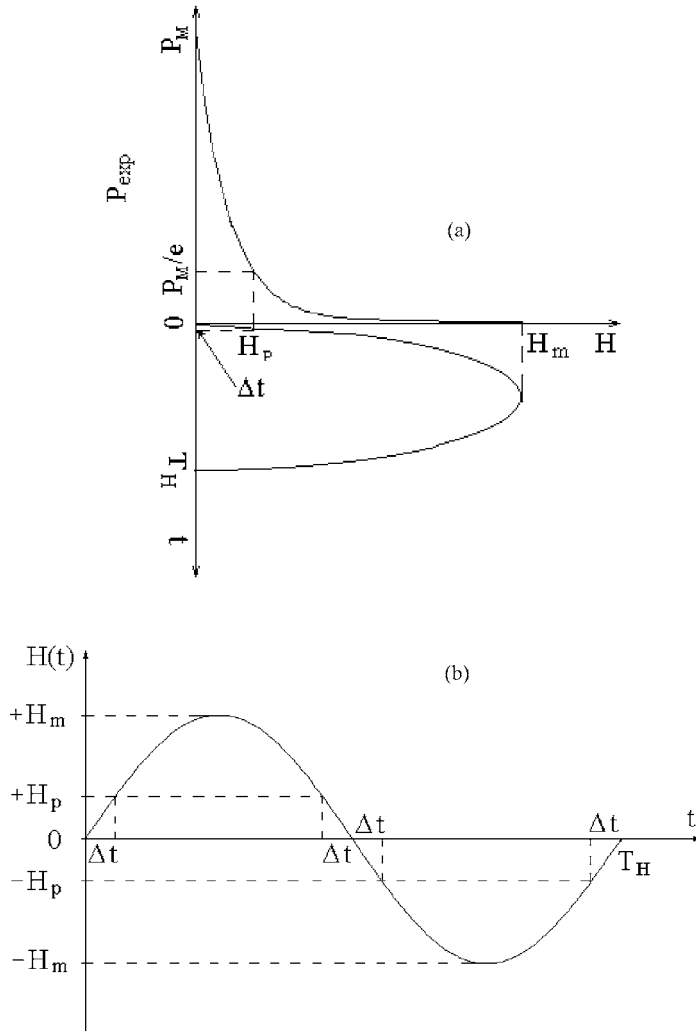


Figure 2. (a) Dependence of the exponential function P_{exp} on the external magnetic field (during a half-period). (b) Variation over time of the external magnetic field; the diagram also shows the level of the threshold field (H_p) under which the thermal relaxation of magnetization occurs.

is the maximum probability (obtained in the absence of the field), the threshold field is obtained:

$$H_p = \frac{2K_a}{\mu_0 M_s} \left[\left(1 + \frac{6k_B T}{\pi K_a d_m^3} \right)^{1/2} - 1 \right], \quad (23)$$

below which the magnetic moments can relax. Equation (23) can also be written in a restrained form:

$$H_p = H_K \left[\left(1 + \frac{k_B T}{K_a V_m} \right)^{1/2} - 1 \right]. \quad (24)$$

The equation makes it possible to determine the value of the external magnetic field below which the effect of the field on the thermal relaxation of the magnetization can be ignored. The value of the threshold field depends, as expected, not only on the anisotropy, but also on the magnetic volume of the nanoparticles and on their temperature, as well as on the relation between the thermal energy ($k_B T$) and the anisotropy energy ($K_a V_m$).

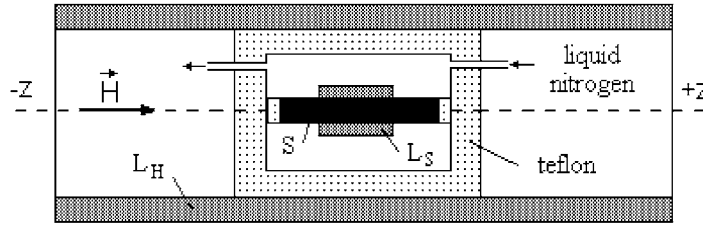


Figure 3. The system for cooling the sample (S), together with the magnetization coil (L_H). L_S is the probe coil in which voltage is induced that is proportional to the magnetization (M) of the sample after the application of the magnetizing field (H); (· · · · ·): the direction of applying the field H is the same as the easy magnetization axis direction ($-z, +z$) (see figure 1) of the system.

However, when the magnetic field varies according to a sinusoidal law in the time t_{mH} the field will reach the value (figure 2(b))

$$H_p = H_m \sin(\omega \cdot t_{mH}) \quad (25)$$

where $\omega = 2\pi/T_H$, T_H is the period of the alternating magnetic field and H_m is the maximum value of the magnetic field. From the last equation, I obtain the time

$$t_{mH} = \frac{T_H}{2\pi} \arcsin\left(\frac{H_p}{H_m}\right) < t_m, \quad (26)$$

during which the magnetic moments can relax (they can pass the energy barrier) in the presence of the magnetic field.

According to what is given above, in the presence of the sinusoidal magnetic field H with a high amplitude ($H_m > H_p$), that is applied along the easy magnetization axis, the measurement time can no longer be considered as being the period T_H of the alternating field ($t_m = T_H$ (equation (8))), but is the time t_{mH} defined by equation (26) where H_p is given by equations (23), (24).

When the external magnetic field is applied in the opposite sense ($\varphi = \pi$), the roles of the magnetic moments will change. Thus, for magnetic moments oriented in the sense opposed to the magnetic field, the energy barrier will decrease, and for those oriented in the same sense as the field, it will increase. When the magnetic field decreases from the value corresponding to saturation to zero, the results obtained above still apply.

3. Experimental details

The theory presented in section 2 was verified for a ferrofluid-type sample [22] made up of magnetite nanoparticles that were quite spherical, isolated (surfacted with oleic acid) and dispersed in kerosene. The colloidal particles were obtained by the chemical co-precipitation method. Finally, the ferrofluid was filtered in a magnetic field gradient, thus providing a good stability over time. The alignment of the nanoparticles (and together with them their easy magnetization axes) in the direction where the alternating magnetization field was to be applied has been obtained by placing the sample at room temperature in a continuous magnetic field (150 kA m^{-1}) that saturated the sample (figure 3) and then by cooling it down to the temperature of liquid nitrogen. Thus, apart from the alignment of the nanoparticles, their fixing in space was also obtained by freezing the carrier fluid. After removing the continuous magnetic field, the sample was magnetized at a temperature of 77 K in an alternating (sinusoidal) field (H) with an amplitude $H_m = 10^5 \text{ A m}^{-1}$. The magnetization curve that was

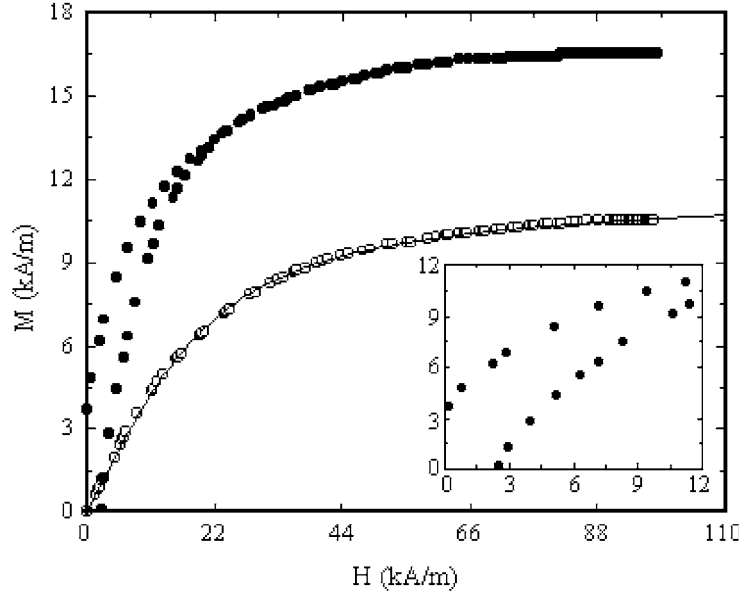


Figure 4. Magnetization curves of the sample recorded at the temperature of liquid nitrogen (●) and at room temperature (○); (—): Langevin curve. Inset: magnified image around the origin for the curve (●).

recorded is shown in figure 4, curve (●). The diagram also shows the curve recorded when the nanoparticle system has returned to room temperature (curve (○)); this corresponds to a Langevin-type curve [23] (continuous curve (—)), which shows that at a temperature of 298 K the behaviour of the nanoparticle system is superparamagnetic (SPM). The magnetic packing volume fraction of the sample is $\varepsilon_m = M_{\text{sat}}/M_s = 0.024$, where the saturation magnetization $M_{\text{sat}} = 11.46 \times 10^3 \text{ A m}^{-1}$ was determined by fitting the experimental curve (curve (○)) with the Langevin function (curve (—)) for an infinite field, and the spontaneous magnetization is $M_s = 477.5 \times 10^3 \text{ A m}^{-1}$ [24]. The relatively low value of ε_m means that the distance between the nanoparticles in the ferrofluid is quite high, and the dipolar interactions can be neglected. Moreover, the dipole–dipole coupling parameter [25], given by the ratio between the maximum energy of interaction between the magnetic moments of two nanoparticles approximated as being spherical and the thermal energy $k_B T$,

$$\lambda = (\mu_0 \pi M_s^2 / 144 k_B T) (\langle d_m \rangle^2 / \langle d_h \rangle)^3, \quad (27)$$

has a value of 0.53. In equation (27), $\langle d_m \rangle = 10.86 \text{ nm}$ [22] is the mean magnetic diameter of the nanoparticles and $\langle d_h \rangle = \langle d \rangle + 2\langle \delta \rangle$ is the hydrodynamic diameter ($\langle d \rangle = 12.7 \text{ nm}$ [22] is the physical diameter and $\langle \delta \rangle \sim 2 \text{ nm}$ is the average length of the chain in the oleic acid (surfactant) molecule). Previous studies have shown that thermodynamically stable particle clusters are formed for $\lambda > 1$, but closer to the values 2–4.5 [26–28]. Since in the case of our ferrofluid $\lambda = 0.53 < 1$, it results that thermal agitation successfully opposes the formation of particle clusters.

In the presence of the external magnetic field, even if the Langevin parameter (dipole–field interaction parameter),

$$\xi = \mu_0 \pi M_s \langle d_m \rangle^3 H / 6 k_B T, \quad (28)$$

reaches values >5 when the field increases towards its saturation value, the conditions for the formation of thermodynamically stable chains $\lambda \gg 1$ and $\lambda \gg \xi$ (according to the statistic model suggested by Zubarev [29]), are not met, since parameter λ in our case is relatively low. Additionally, in [30] it was shown that at $\varepsilon_m = 0.01$, for $\lambda < 4$ and $\xi \leq 5$, no particle chains are formed; only for $\lambda \sim 6-8$ is their formation influenced positively by an increase of the field. This means that even if particle clusters are formed at strong fields, they are not stable aggregates and they only have a short lifetime.

At a temperature of 77 K, since the nanoparticles are fixed in the solid matrix, the formation of clusters under the effect of the external magnetic field is out of the question. In conclusion, in the case of our ferrofluid it is reasonable to consider neglecting interactions that lead to the formation of clusters that are thermodynamically stable. At the temperature of liquid nitrogen there is a very large deviation of the experimental curve (\bullet) ($M_r = 3.6 \times 10^3 \text{ A m}^{-1}$ (M_r —remanent magnetization)) and $H_c = 2.6 \times 10^3 \text{ A m}^{-1}$ (H_c —coercive field; see the inset) from the Langevin curve ($M_r = 0$, $H_c = 0$), a deviation that is reflected in the existence of the remanence $r = 0.21$. The value of the experimental remanence suggests an approach of the magnetic relaxation time to the measurement time, since the process is dynamic (the frequency of the alternating field is of 50 Hz). The observed remanence will be explained below and the theoretical results presented in the previous section will be compared to those obtained experimentally.

4. Discussion

Figure 5(a) shows the variation of the nanoparticle's energy as a function of angle φ and field H , calculated for a temperature of 77 K. For the representation I have used: $\langle d_m \rangle = 12.35 \text{ nm}$ (value previously determined in [22]) and the effective anisotropy constant $K_a = 12.2 \times 10^3 \text{ J m}^{-3}$ [31], where both values were determined at the same temperature (77 K). The effective anisotropy constant was determined with the equation $K_a = 6k_B T \ln(\tau_{\text{exp}}/\tau_0)/\pi \langle d_m \rangle^3$, where $\tau_{\text{exp}} = 86 \mu\text{s}$ [31] is the relaxation time measured experimentally at a temperature of 77 K for the nanoparticle system with the anisotropy axes aligned in the direction of the field H . From the diagrams (a₁), (a₂), (a₃) (figure 5(a)) it can be observed that the energy barrier increases with increase of the magnetic field and the maximum of the barrier shifts toward values of the φ angle that are higher than 90° . Figure 5(b) is a representation of the energy variation for the values of the magnetic fields 0, 30 and 100 kA m^{-1} . When the magnetic field decreases from the saturation value (100 kA m^{-1} ; diagram (b₃)) to 0 (diagram (b₁)), the barrier energy for the magnetic moments (oriented in the sense of the field) will decrease gradually and the probability of the magnetic moments passing the energy barrier will increase (figure 6). As has been shown in the previous section, when field H decreases and reaches the threshold value H_p , the barrier energy will have a value that will allow some (since in the real system there is a distribution of the nanoparticle diameters) magnetic moments to pass the energy barrier. But during the time t_{mH} , when the field reaches the threshold value and then decreases to 0, the thermal agitation does not have sufficient time to invert all magnetic moments of the $n/2$ particles. Thus, even at $H = 0$, there will be a surplus

$$\Delta n = n - 2n_0 \quad (29)$$

of magnetic moments oriented in the initial sense of the field, which will imply a remanent magnetization (figure 4, curve (\bullet)). In equation (29) n_0 is the number of magnetic moments (from the volume unit) that were inverted by 180° along the easy magnetization axis (figure 5(b₁)). The concentration percentage of these can be determined, having in view the value of the experimental remanence, $r = M_r/M_{\text{sat}} = 0.21$, which can also be expressed by the

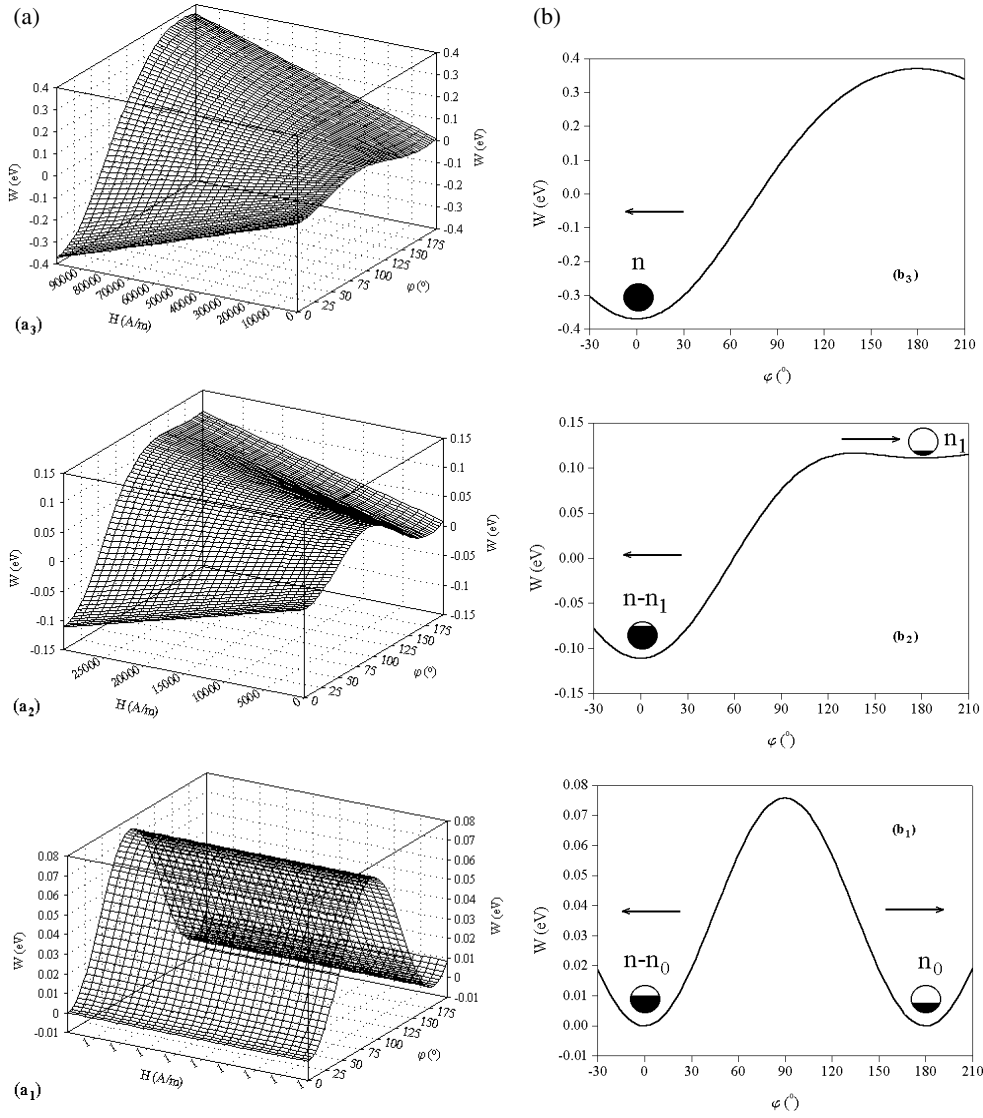


Figure 5. (a) Variation of the nanoparticle's energy (expressed in eV) as a function of the angle φ and the field H , for $H = 1 \text{ A m}^{-1}$ (a₁) and when H increases: from 1 to the maximum value H_m , i.e. $30 \times 10^3 \text{ A m}^{-1}$ (a₂), and $100 \times 10^3 \text{ A m}^{-1}$ (a₃), respectively. (b) Modification of the barrier energy (W_b) and of the magnetic moment population (n) for the maximum values of the field, namely 0 A m^{-1} (b₁), $30 \times 10^3 \text{ A m}^{-1}$ (b₂) and $100 \times 10^3 \text{ A m}^{-1}$ (b₃).

following equation:

$$r = \frac{n - 2n_0}{n} = \frac{\Delta n}{n}. \quad (30)$$

Here we had in view that the saturation magnetization M_{sat} and the remanent magnetization M_r can be represented by the equations

$$M_{\text{sat}} \cong nm_p, \quad M_r \cong (n - 2n_0)m_p. \quad (31)$$

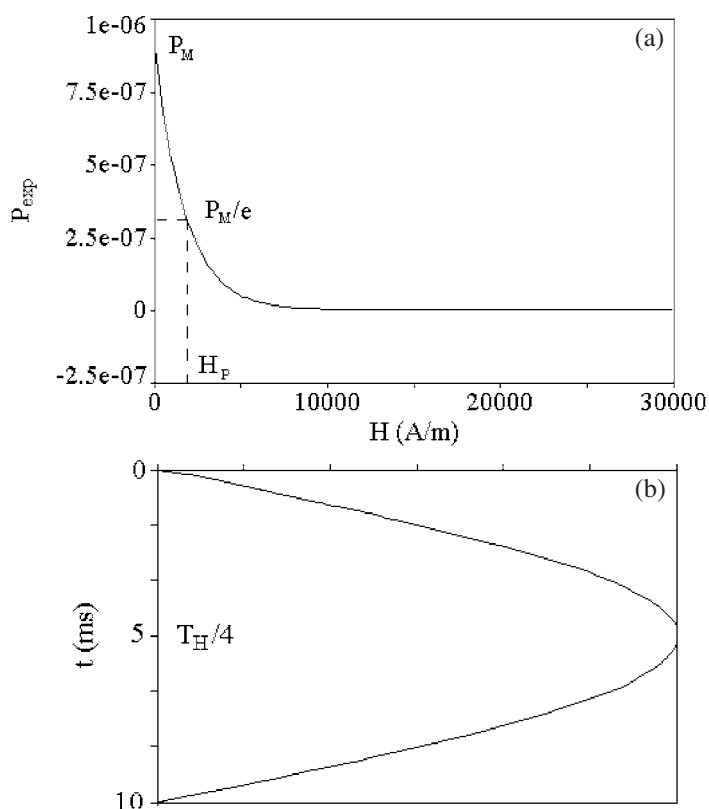


Figure 6. (a) Experimental P_{exp} as a function of the field H ; (b) variation of H over time ($H_m = 30 \times 10^3 \text{ A m}^{-1}$, $t = T_H/2 = 10 \text{ ms}$).

Thus, in agreement with equation (30) it results that only 39.5% of the n magnetic moments (figure 5(b₃)) were inverted by 180° , and the rest ($n - n_0$; figure 5(b₁)) of the 60.5% have retained their orientation. The remanence (figure 4(●)) will be determined in this case by the difference of 21% that represents the magnetic moments that have not been compensated.

If we perform a quantitative analysis of the relaxation processes for magnetization, we can say that at the temperature of liquid nitrogen—since the ferrofluid is frozen—the Brownian rotary diffusion is stopped (the nanoparticles are fixed in space), and $\tau_B \rightarrow \infty$. Under these conditions, according to equation (4), it results that $\tau = \tau_N$ and the relaxation of magnetization only occurs through the Néel process. If we now replace the known values for our case, in equation (23), we obtain $H_p = 1.76 \times 10^3 \text{ A m}^{-1}$ and then from equation (26) it results that $t_{mH} = 56 \mu\text{s}$. The value obtained for t_{mH} is comparable to that of the Néel relaxation time τ_{exp} ($86 \mu\text{s}$) determined experimentally. Moreover, if we consider the limit for H_p to be $\sim 4 \times 10^3 \text{ A m}^{-1}$, as can be seen in figure 6 (when all magnetic moments can actually no longer relax, the probability being practically zero), we obtain $t_{mH} \sim 127 \mu\text{s}$, a value higher than the relaxation time, but quite close to it. In this way, the result obtained for the measurement time using equation (26), where H_p is determined by equation (23), is in good agreement with the experimental result. Since the measurement time is quite close to the relaxation time, this will explain the large remanence (0.21) recorded experimentally (figure 4, curve (●)). The value of the remanence is also (slightly) influenced by the existence of the distribution of the nanoparticle diameters in the real system. The facts shown above apply for $H = 0$ or in a weak field, when equation (2) can still be used. In intense fields, according to equations (1), (4)

and (20), respectively, the relaxation time can be written as

$$\tau = \tau_N = \tau_0 \exp \left[\frac{\pi K_a d_m^3}{6k_B T} \left(1 + \frac{\mu_0 M_s H}{2K_a} \right)^2 \right], \quad (32)$$

and it will increase rapidly with H , which will lead to the condition $\tau_N \gg t_{mH}$ being met. For example, by calculating the relaxation time for a field equal to the threshold field limit ($\sim 4 \text{ kA m}^{-1}$), we obtain $\tau_N \sim 850 \mu\text{s}$. The value obtained (much higher than the measurement time) shows that the magnetic moments are blocked, a result in agreement with the experimental one.

If we were, however, to consider that the measurement time is $t_m = T_H = 20 \text{ ms}$ ($T_H = 1/\nu$, $\nu = 50 \text{ Hz}$), then for $H = 0$ we would obtain τ_N ($86 \mu\text{s}$) $\ll t_m$ (τ_N is $\sim 2.3 \times 10^2$ times smaller than t_m), and the remanence, under these conditions, would tend to zero, a result in contradiction with the one obtained experimentally (see figure 4, curve (●)).

On the other hand, if we use t_{mH} given by equation (26) (where H_p is given by equation (23)) and equation (9) (where $T_H = 1/\nu$), we obtain the blocking temperature

$$\langle T_B \rangle = \pi K_a \langle d_m \rangle^3 \left\{ 6k_B \ln \left[\frac{1}{2\pi \nu \tau_0} \arcsin \left(\frac{H_p}{H_m} \right) \right] \right\}^{-1}. \quad (33)$$

If we assume $K_a \sim 12.2 \times 10^3 \text{ J m}^{-3}$ and $\langle d_m \rangle \sim 12.3 \text{ nm}$ (in the proximity of the temperature of liquid nitrogen these values change slightly), for H_m of 50 kA m^{-1} it results that: $\langle T_B \rangle_{50} \sim 74 \text{ K}$ at 50 Hz , and $\langle T_B \rangle_{640} \sim 95 \text{ K}$ at 640 Hz . These values are in good agreement with the values obtained experimentally, corresponding to the peaks of the curves $M(T)$ obtained in the ac measuring field H_m , for the same frequencies (see figure 7(a)). In addition, if we calculate the blocking temperature (equation (33)) for several frequencies in the range of 20 – 680 Hz , we obtain the curve in figure 7(b), which shows that there is a shift of T_B towards higher temperatures with the increase of frequency. This result is confirmed experimentally by a shifting of the peaks of the curves in figure 7(a) when the frequency increases. In conclusion, the results obtained confirm the validity of the formulae established for the threshold field H_p (equation (23)) and the measurement time in the presence of the high field t_{mH} (equation (26)).

An additional confirmation can be considered: the calculation made at a temperature of 298 K , at which the magnetic behaviour of the aligned nanoparticle system is similar to that shown in figure 4, curve (O) (superparamagnetic). Thus, admitting an anisotropy constant of $\sim 4 \times 10^4 \text{ J m}^{-3}$ (obtained by extrapolation) [31], the threshold field $\sim 10 \text{ kA m}^{-1}$ is obtained, corresponding to a magnetic diameter of 10.86 nm [22]. In this case it results that $t'_{mH} \sim 320 \mu\text{s}$. At room temperature, where the ferrofluid goes over into the liquid state, both relaxation processes that are coupled can contribute to the relaxation of the magnetization. In low fields, when $\xi \ll 1$ —a condition well met for $H \leq 1 \text{ kA m}^{-1}$ —the equations (2) and (3) can be used for calculating the relaxation times. In this way, if we replace the known values, it results that $\tau_N = 0.66 \mu\text{s}$ and $\tau_B = 13.3 \mu\text{s}$. In the calculation we have used $\eta = 7543 \times 10^{-6} \text{ kg m}^{-1} \text{ s}^{-1}$ [32] and $V = \pi d_h^3/6$. Since the condition τ_N ($0.66 \mu\text{s}$) $\ll \tau_B$ ($13.3 \mu\text{s}$) $\ll t'_{mH}$ ($320 \mu\text{s}$) is met, in this case the relaxation of magnetization will only occur through Néel processes and the relaxation time—according to equation (4)—is $\tau \simeq \tau_N = 0.66 \mu\text{s}$. In intense fields, we also have to consider the value of the anisotropy field [12], which in this case is $H_K = 133.4 \times 10^3 \text{ A m}^{-1}$. For fields that are appreciably lower than H_K , but are still intense (e.g. 40 kA m^{-1}), for the calculation of the relaxation time of the particle orientation we can use equation (5) to obtain an approximate value, and for the Néel relaxation time we can use equation (32) (in the field considered, the nanoparticles are quite well oriented (see figure 4, curve (O))). If we make a calculation,

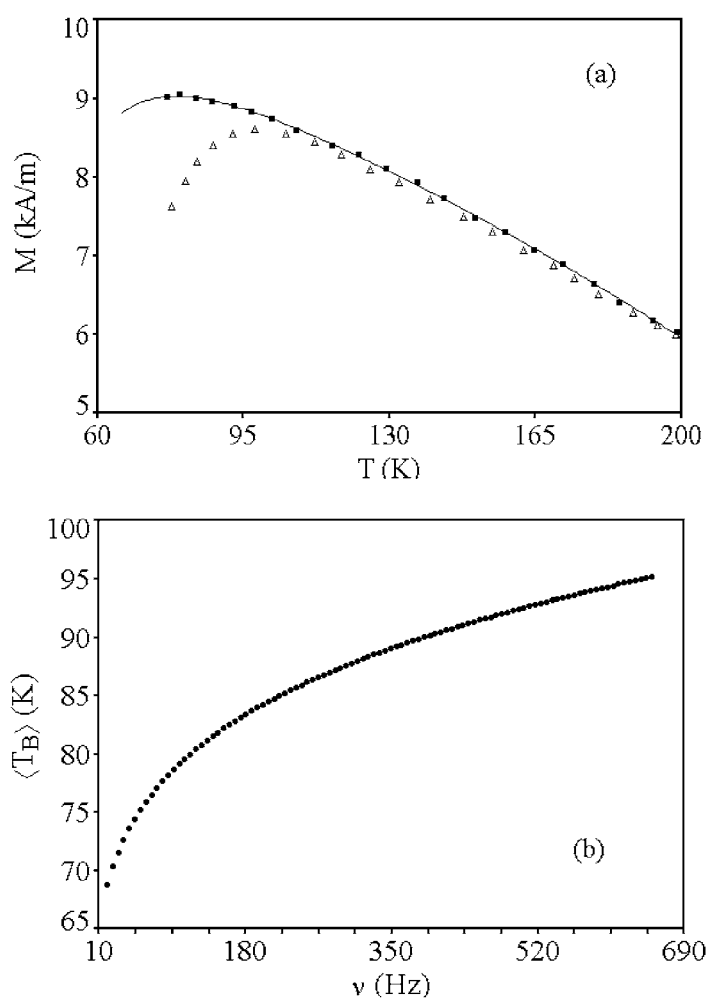


Figure 7. (a) Magnetization versus temperature recorded at a frequency of 50 Hz (\bullet) (—, fit function) and 640 Hz (Δ), respectively. (b) Variation of the blocking temperature with frequency.

we obtain $\tau_n \sim 6.8 \mu\text{s}$ and $\tau_N \cong 61 \mu\text{s}$. According to this result—since in this case the condition $\tau_n (6.8 \mu\text{s}) \ll \tau_N (61 \mu\text{s}) \ll t'_{\text{mH}} (320 \mu\text{s})$ is met—we can state that in intense fields, the relaxation of magnetization occurs exclusively by an orientation of the particles and the corresponding relaxation time is $\tau \cong \tau_n = 6.8 \mu\text{s}$. In the area of transition from high fields to low fields, both processes will contribute to the relaxation of magnetization and the relaxation time can be determined with equation (4): of the order of 10^{-6} s. From the facts discussed it must be observed that at a temperature of 298 K, the condition of the relaxation time (τ_n for strong fields, τ in the transition area or τ_N for low fields) being much lower than the measuring time $t'_{\text{mH}} (320 \mu\text{s})$ is always met. This result is in good agreement with the experimental curve (figure 4, curve (O)), which shows that the magnetic moments follow almost instantly the variation of the external magnetic field (the experimental curve follows a Langevin-type function).

In conclusion, the theoretical results obtained are validated by the experimental data, which explains the observed magnetic behaviour, both at a temperature of 77 K and at 298 K.

Recently, Fannin *et al* [33] have shown that an external (polarization) magnetic field also influences the frequency dependence (in the range 100 MHz–6 GHz) of the components of the

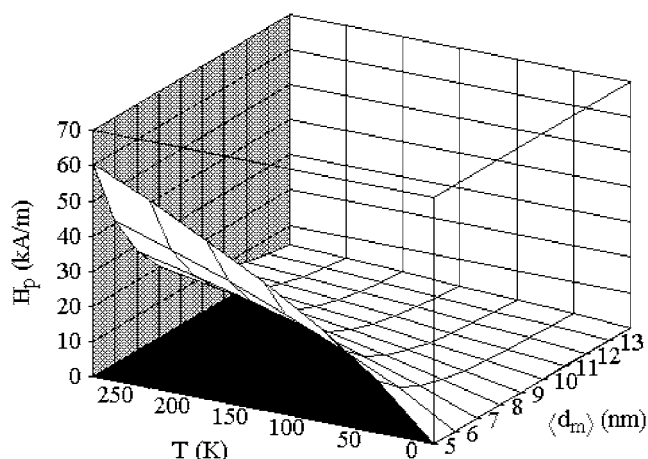


Figure 8. 3D (spatial) variation of the threshold field as a function of the magnetic diameter and the nanoparticle temperature.

complex magnetic susceptibility χ' and χ'' (χ' is the real part and χ'' is the imaginary part of the susceptibility) of a concentrated ferrofluid, with magnetite particles dispersed in kerosene, with a magnetic diameter of 8.5 nm and a concentration of $30 \times 10^{16} \text{ cm}^{-3}$. The authors have shown that as the external magnetic field increases from 0 to 1.3 kOe ($\sim 100 \text{ kA m}^{-1}$), the frequency corresponding to the maximum of component χ'' (f_{max}) and the one corresponding to resonance (f_{res} ; the frequency when component χ' passes through zero) shift towards higher values; at the same time, the two frequencies (f_{max} and f_{res}), which are different at low fields ($f_{\text{max}} < f_{\text{res}}$), get closer to each other as the field increases, until they coincide ($f_{\text{max}}/f_{\text{res}} = 1$) at high fields ($\sim 100 \text{ kA m}^{-1}$).

Next, we will show that the equations found for H_p (equation (23)) and t_{mH} (equation (26)) correspond to physical reality. For this purpose, we have calculated the field H_p at various temperatures (figure 8), considering a temperature range of 0–300 K; at the same time, we have considered other values of the magnetic diameter, both lower and higher than $\langle d_m \rangle$ ($5 < \langle d_m \rangle < 14 \text{ nm}$; values seen more often in practice). When $T \rightarrow 0 \text{ K}$, the field $H_p \rightarrow 0$, which implies that the magnetic moments can no longer relax, not even in the case of very small nanoparticles. The same result is obtained when $H_m \rightarrow \infty$. At high temperatures, however, the values of H_p become considerable (figure 8), especially in the case of small nanoparticles (e.g. $H_p = 60 \text{ kA m}^{-1}$, at a temperature of 300 K and a diameter of 5 nm). In this case, t_{mH} will increase very much, reaching for example $\sim 2 \text{ ms}$ at a diameter of 5 nm (at $H_m = 100 \text{ kA m}^{-1}$ and $T_H = 20 \text{ ms}$). Naturally, the value of t_{mH} will also depend on the amplitude of the external magnetic field (H_m) and its frequency. Figure 9 shows the variation of t_{mH} as a function of H_m for $H_p = 1.76 \text{ kA m}^{-1}$ and $T_H = 20 \text{ ms}$. Equation (26) applies as long as the condition that H_m is higher (or much higher) than H_p is met. (i) When $H_m \rightarrow \infty$, the time $t_{\text{mH}} \rightarrow 0$. (ii) At the limit, when $H_m = H_p$, from equation (26) it results that

$$(t_{\text{mH}})_1 = \pi/2\omega = T_H/4 \quad (34)$$

i.e., the measurement time in this case can be considered the time range that equals a quarter (5 ms) of the period of the alternating magnetic field (see the inset of figure 9). (iii) Still, when H_m becomes lower than H_p , equation (26) becomes impossible since the sine function cannot have values higher than 1. Physically, it must be understood that in this situation we can no longer speak of a time range when the magnetic moments can relax, but they can relax during the whole period T_H of the alternating field. As a result, at low amplitude of the magnetization field (in our case for $H_m < H_p = 1.76 \text{ kA m}^{-1}$ (or $H_m < 22.1 \text{ Oe}$ in the CGS units system)),

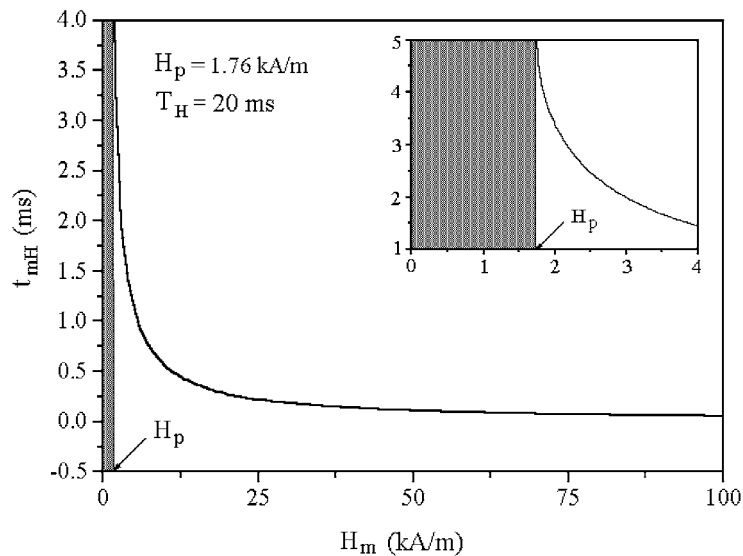


Figure 9. Dependence of the measurement time on the applied field. Inset: representation on an enlarged scale around the threshold field H_p .

the magnetic moments can relax under the effect of thermal activation for the whole period of the alternating field. Hence, in this case we can consider the measurement time as being the period T_H ($t_{mH} = T_H = t_m$). This result is in agreement with the one already known [14, 15], when in magnetic fields with *low amplitudes* the measurement time is considered to be $t_m = T_H$ (equation (8)).

In conclusion, as has already been shown above, when H becomes significant and exceeds the threshold value (H_p), the condition $t_m = T_H$ can no longer be used, since it is not realistic. In this case, the contribution of the magnetic field to the energy barrier has to be taken into consideration and as the time for observing the magnetic relaxation process (measurement time) the time t_{mH} given by equation (26) has to be used. At the same time, according to equation (26), the measurement time t_{mH} will depend at a given period of the magnetic field not only on H_p , but also on the amplitude of the external magnetic field H_m .

In addition to the facts described above, it also has to be mentioned that considering t_{mH} to be the measurement time will lead to important corrections to the value of the magnetic anisotropy constant or to the volume of the nanoparticles (equation (9)) when these values are determined experimentally under dynamic conditions imposing the equation $\tau = t_{mH}$ when the external magnetic field exceeds the threshold value, instead of $\tau = t_m = T_H$, as usual.

5. Conclusions

In the presence of an alternating (harmonic) external magnetic field with a high amplitude, applied along the direction of the easy magnetization axis of a system of aligned nanoparticles, the remanence of the system is determined dynamically and it will depend at a given period of the magnetic field both on the amplitude of the applied magnetic field (H_m) and on the threshold field (H_p); the remanence of the system of aligned nanoparticles is due to the blocking of the magnetic moments of the nanoparticles. The field H_p depends on the nature and volume of the nanoparticles, and on the temperature. Its value will increase as the volume of the nanoparticles decreases and the temperature increases. When there is a decrease of the external magnetic field that has oriented all the magnetic moments of the nanoparticles along the direction and

in the same sense as the applied magnetic field, as long as the amplitude of the magnetic field is higher than the value of the threshold field ($H_m > H_p$), the time during which the magnetic moments can relax is smaller than the period of the alternating field ($t_{mH} < T_H$). If the amplitude of the external magnetic field decreases to under the value corresponding to the threshold field ($H_m < H_p$), the relaxation will occur throughout the whole period of the alternating magnetic field ($t_{mH} = t_m = T_H$), a result in agreement with the one already known. The measurement time t_{mH} (in the presence of the high alternating field) will depend at a given frequency on H_p and H_m .

The theoretical analysis carried out for a system of aligned isolated nanoparticles is confirmed by the experimental results obtained in the case of a ferrofluid-type system made up of magnetite nanoparticles covered in oleic acid, aligned and fixed in space by freezing in liquid nitrogen.

These are very important aspects that have to be taken into consideration (when the volume of the nanoparticle is lower than the critical volume above which the magnetization of the nanoparticle is stable), having in view that in practical applications of these nanomaterials, most of the time an external magnetic field is applied.

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