ISSN: 2755-0168

Journal of Biotechnology & Bioinformatics Research

SCIENTIFIC Research and Community

Review Article

Open Access

Super-Antiferromagnetics Nanoparticles for Magnetic Hyperthermia Applications: Effect of the Dc and Ac Magnetic Field

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ABSTRACT

The importance of magnetic hyperthermia cancer treatments is based on the magnetic characteristic of the nanoparticles and their dependence on the DC and AC magnetic fields. In this paper we Study the dynamic magnetic hysteresis (DMH) of Super Antiferromagnetic nanoparticle, we use Brown's continuous diffusion model to we evaluate the hysteresis loops, for extensive ranges of the anisotropy, the ac and dc magnetic fields.

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Received: August 25, 2020; **Accepted:** September 07, 2020, **Published:** September 11, 2020

Introduction

Magnetic particle hyperthermia is the most significant of the currently known biomedical application of magnetic nanoparticles [1-3]. It's based on the dissipation in the form of heat induced by magnetic nanoparticles under the influence of an external high frequency magnetic field. Significant progress has been made to make the material properties, optimal for this application. Indeed, reducing the size of materials down to the nanometric scale can induce new physicochemical properties, which makes the study of these materials interesting not only from the fundamental point of view but also from the application point of view. Single domain ferromagnetic nanoparticles are characterized by instability of the magnetization M(t) due to thermal agitation, this instability produce spontaneous change of particle orientation from metastable state to another resulting in the phenomenon of superparamagnetism [4-7]. Furthermore, due to the important magnetic dipole moment of nanoparticles, the Zeeman energy is large even in relatively weak external magnetic fields. Thus, the magnetization reversal has a strong field dependence causing nonlinear effects in the dynamic magnetic hysteresis, etc. In the case of antiferromagnetic nanoparticles, the behavior of the magnetization differ from those of ferromagnetic ones because of the intrinsic properties of antiferromagnetic materials. The magnetic behavior of *antiferromagnetic* nanoparticles can be different from that observed in the bulk, e.g., enhanced magnetic moment and coercivity, exchange bias, increase in magnetic moment with temperature, decrease in the susceptibility with temperature below the ordering (Néel) temperature T_N and its enhancement compared to that of the bulk. The basic theory of antiferromagnetic nanoparticles was described by Néel, he concluded, in particular, that total magnetic compensation of the sublattices in antiferromagnetic nanoparticles is impossible for a number of reasons, namely, unequal numbers of spins in crystal planes, spin frustration near the surface, lattice defects, etc. Hence, an equilibrium magnetization should obtain in such particles; moreover, they should become superparamagnetic at a finite temperature just as ferromagnetic nanoparticles. According to Néel, the so-called super antiferromagnetism arises in a nanoparticle with an even number of sublattice planes, causing an appreciable increase in transverse susceptibility in comparison to that of a massive sample. Indeed measurements on ferritin and ferrihydrite showed that the effective bulk susceptibility of these particles exceeds that of a macrocrystal by a factor of 2 or 3. Subsequently, the effective spontaneous magnetization of antiferromagnetic nanoparticles ranges from several tenths to several units of gauss, i.e., it is of the same order of magnitude as the magnetization of weak ferromagnets [8-10]. The first theory of thermal fluctuations of magnetic nanoparticles was initiated by Néel after that [4-6], Brown used the classical theory of transition states to describe the evolution of magnetization, known as Néel-Brown model Its treatment uses the classical theory of Brownian motion with the Landau-Lifshitz-Gilbert equation augmented by random fields considered as the Langevin magnetic equation governing the dynamics of stochastic magnetization [11-13]. At temperatures below TN, this model can be adapted to antiferromagnetic nanoparticles. In the simplest case, give the magnetic moments of the sub-networks and of an antiferromagnetic particle subjected to a continuous magnetic field [8].

$$\mathbf{m}_{1,2} = \mathbf{u}\left[\frac{\mu}{2} \pm vM_S - \frac{v\chi_A}{2}(\mathbf{u}\cdot\mathbf{H}_0)\right].$$

Here M_s is the bulk sublattice magnetization, χ_A is a parameter characterizing the induced magnetic moment of the particle, $\mathbf{u} = (\mathbf{m}_1 - \mathbf{m}_2)/(2vM_s)$ is the unit vector along the decompensation magnetic moment $\boldsymbol{\mu} = \mathbf{u}\mu$, and v is the particle volume, the magnetic moment dynamics of uniaxial antiferromagnetic nanoparticles are governed by a Fokker-Planck equation for the distribution function $W(u, t)$ of magnetic moment orientations on a unit sphere, viz., [8,11].

$$2\tau_N \frac{\partial W}{\partial t} = \frac{\beta}{\alpha}\mathbf{u}\cdot(\nabla V \times \nabla W) + \nabla\cdot(\nabla W + \beta W \nabla V), \quad (1)$$

Where $\nabla = \partial / \partial \mathbf{u}$ is the gradient operator on the unit sphere, $\tau_N = \tau_0(\alpha + \alpha^{-1})$ is the characteristic free diffusion time, $\tau_0 = \beta\mu_0\mu / (2\gamma)$ $\beta = 1/(kT)$ k is Boltzmann's constant, T is the absolute temperature, γ is gyromagnetic ratio, and α is the dimensionless dissipation parameter. The dimensionless free-energy $\beta V(\vartheta, \varphi, t)$ of a uniaxial antiferromagnetic nanoparticle in superimposed magnetic dc and ac fields $\mathbf{H}_0 + \mathbf{H}\cos\omega t$ *is* given by [8,14].

$$\beta V(\vartheta,\varphi,t) = \sigma \sin^2\vartheta - (\gamma_1 \sin\vartheta\cos\varphi + \gamma_2 \sin\vartheta\sin\varphi + \gamma_3\cos\vartheta)\xi(t) + \frac{\zeta}{2}(\gamma_1 \sin\vartheta\cos\varphi + \gamma_2 \sin\vartheta\sin\varphi + \gamma_3\cos\vartheta)^2\xi^2(t). \quad (2)$$

Here ϑ and φ are the polar and azimuthal angles, $\sigma = v\beta K$ is the dimensionless anisotropy parameter, K is the anisotropy constant, v is the volume of the particle,
$\xi(t)\ \xi_0 + \xi\cos\omega t$

$\xi_0 = \beta\mu_0\mu H_0$ and $\xi = \beta\mu_0\mu H$ is the applied field parameter, $\zeta = v\chi_A / \beta\mu_0^2\mu^2$ is the "antiferromagnetic" parameter, and $\gamma_1 = \sin\psi\cos\phi$, $\gamma_2 = \sin\psi\cos\phi$, $\gamma_3 = \cos\psi$ are the direction cosines of the vectors $\mathbf{H}_0$ and $\mathbf{H}$, which are assumed parallel. In the absence of the ac driving field, $\xi = 0$, the free energy, Eq. (2), has a bistable structure with two minima in the north and south polar regions separated by a potential barrier with a saddle point in the equatorial region [14]. For a particular case $\psi = 0$, the free energy, Eq. (2), becomes axially symmetric. The free energy from Eq. (2) for $\zeta = 0$ reduces to that for uniaxial ferromagnetic nanoparticles. The extra ζ-term in Eq. (2) affects significantly the dynamics of the magnetic moment in the presence of an ac driving field.

Apart from certain studies, the passage between linear and nonlinear regimes has not yet been explored in detail in the context of antiferromagnetic particles. Most of the articles focused either exclusively on the theory of linear response or the other extreme high field amplitudes. For magnetic hyperthermia, the latter is not very interesting given that such high fields are both dif fi cult to achieve in the laboratory and possibly dangerous for the patient. It is also known both experimentally and theoretically than the linear regime is in fact an asymptotic approximation to the limit of zero field amplitude so that even small fields should already exhibit measurable non-linearities.

The goal of this paper is to give a detailed study of the effect of DC and the AC magnetic field on the Dynamic magnetic Hysteresis of Super-antiferromagnetic nanoparticles. A theoretical study of magnetic hyperthermia therefore leads us to dynamic hysteresis calculations using an easy model capable of explaining damping mechanisms. For example, in this article we use Néel-Brown theory. This approach is both easy and very suitable, allowing calculating the response to any amplitude or frequency of field with good precision. However, and within the framework of the nonlinear response, no analytical solution is available for the moment, obliging to resort exclusively to numerical calculations.

Numerical Calculation

Now, the task of calculating ac stationary nonlinear responses of the magnetization from the Fokker-Planck equation (1) can always be reduced to the solution of an infinite hierarchy of differential-recurrence equations for the statistical moments $\langle Y_{lm}\rangle(t)$ (averaged spherical harmonics) governing the magnetization dynamics [15,18].

$$\tau_N \frac{d}{dt}\langle Y_{lm}\rangle(t) = \sum_{r,s} e_{l,m,l+r,m+s}(t)\langle Y_{l+rm+s}\rangle(t) \quad (3)$$

Here the angular brackets $\langle\ \rangle$ mean statistical averaging, $Y_{lm}(\vartheta, \varphi)$ are the spherical harmonics given by [19]

$$Y_{lm}(\vartheta,\varphi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} e^{im\varphi} P_l^m(\cos\vartheta),$$

and $P_l^m(x)$ are the associated Legendre functions [19]. For the free energy potential defined by Eq. (2), the differential-recurrence relation Eq. (3) reduces to an infinite hierarchy of 25-term differential-recurrence relation for the statistical moments $\langle Y_{lm}\rangle(t)$ [see Appendix for details].

Henceforth, we shall assume without loss of generality that the vectors $\mathbf{H}_0$ and $\mathbf{H}$ lie in the XZ-plane of the laboratory coordinate system, i.e., $\phi = 0$, so that the direction cosines are $\gamma_1 = \sin\psi$, $\gamma_2 = 0$, $\gamma_3 = \cos\psi$.

Now by confining ourselves to the stationary solution for the average magnetic moment of the particle in the direction of the ac driving field $\mu_H(t) = \mu\langle\cos\Theta\rangle(t)$, where Θ is the angle between the vectors $\boldsymbol{\mu}$ and $\mathbf{H}$ so that

$\cos\Theta = \cos\psi\cos\vartheta + \sin\psi\sin\vartheta\cos\varphi$ and using the known definitions of the spherical harmonics of the first rank, viz [19].

$$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\vartheta, \quad Y_{1\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\vartheta e^{\pm i\varphi}, \quad (4)$$

We see that $\mu H(t)$ may be formally expressed via the statistical moments $\langle Y_{10}\rangle(t)$ and $\langle Y_{11}\rangle(t)$ as

$$\mu_H(t) = \mu\sqrt{\frac{4\pi}{3}}\left\{\cos\psi\langle Y_{10}\rangle(t) - \sqrt{2}\sin\psi\,\mathrm{Re}\left[\langle Y_{11}\rangle(t)\right]\right\} \quad (5)$$

Now, since we deal with the stationary ac response, which is independent of the initial conditions, we need only the steady state solution of Eq. (3) so that $\mu_H(t)$ can be expanded as a Fourier series, viz.

$$\mu_H(t) = \mu\sum_{k=-\infty}^{\infty} m_1^k(\omega)e^{ik\omega t} \quad (6)$$

Where $m_1^k(\omega)$ is the amplitude of the k^{th} harmonic in the nonlinear response given by [18] [cf. Eq. (8) of that paper]

$$m_1^k(\omega) = \sqrt{\frac{4\pi}{3}}\left[\cos\psi c_{10}^k(\omega) + \sin\psi\frac{c_{1-1}^k(\omega) - c_{11}^k(\omega)}{\sqrt{2}}\right]. \quad (7)$$

The $c^k_{l,m}(\omega)$ are the coefficients in the time Fourier series development of the averaged spherical harmonics $\langle Y_{lm}\rangle(t)$, viz.,

$$\langle Y_{lm}\rangle(t) = \sum_{k=-\infty}^{\infty} c_{lm}^k(\omega)e^{ik\omega t} \quad (8)$$

The Fourier coefficients $c^k_{l,m}(\omega)$ and, thus, $\mu_H(t)$ can then be calculated using matrix continued fractions (see Ref).

Nonlinear effects in the ac stationary response become important for $\xi > 1$. The condition $\xi << 1$ corresponds to the linear response to a weak ac field, where $\mu_H(t)/H$ is independent of the ac field strength.

Furthermore, via $m^1_1(\omega)$ we can calculate the normalized area of the dynamic magnetic hysteresis (DMH) loop A_n, which is the energy loss per particle and per cycle of the ac field, defined as [19]

$$A_n = \frac{1}{4\mu H}\oint \mu_H(t)dH(t) = -\frac{\pi}{2}\mathrm{Im}\left[m_1^1(\omega)\right] \qquad (9)$$

(The phenomenon of DMH in single-domain magnetically *isotropic* nanoparticles was discovered by Ignatchenko and Gekht [19]). The DMH loop represents a parametric plot of the steady-state time-dependent magnetization as a function of the ac field, i.e., $M_H(t) = \mu_H(t)/v$ *vs.* $H(t)=H\cos\omega t$. All other harmonic components $m^k_1(\omega)$ with $k > 1$ may be calculated in a same method. As cited in Refs. [12], the calculation of the nonlinear ac stationary response from the Fokker-Planck Eq. (1) may be reduced to an infinite hierarchy of differential-recurrence equations for the statistical moments $c_{lm}(t) = \left\langle Y_{lm}\left[\vartheta(t),\varphi(t)\right]\right\rangle$ governing the magnetization relaxation. All the details of the calculations are given in the reference [13,15].

Results and Discussion

Normalized DMH loops, i.e., $m(t) = \mu_H(t)/\mu$ vs. $h(t) = H(t)/H = \cos\omega t$, for various value of the damping α = 0.6, 5,12, in low and high frequency $\omega\tau_0 = 10^{-3}$, respectively are presented in Figure.1, [Fig. 1.(a): $\omega\tau_0 = 1$; High Frequency, Fig. 1.(a):Low Frequency: $\omega\tau_0 = 10^{-3}$]. The loops depend strongly the damping. We note that the size of the cycles is proportional with the value of dissipation in the low frequencies whereas it is inversely proportional in the high frequencies. We also note that the cycles take the form of an ellipsoid in the high frequencies

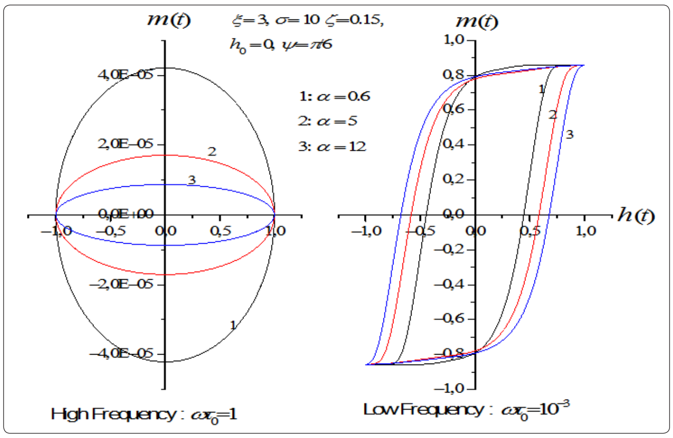

Figure 1: (Color on line) DMH loops for barrier parameter σ = 10, damping α = 0.5, ac field parameter $\xi = 3$, dc field angle $\psi = \pi/6$, and various value of damping α = 0.6, 5,12 in low and high frequency, $\omega\tau_0 = 10^{-3}$ respectively.

The loops depend strongly the dc field parameters $h_0 = \xi_0/(2\sigma)$. This results are Showed in Figure.2. At finite temperatures due to thermal motion, the particle magnetic moment is never completely saturated wandering between the "up" and "down" states. Furthermore, the stationary motion of $\mu_H(t)$ is insensitive to the initial conditions and the shape of DMH loops for given values of anisotropy parameter σ, antiferromagnetic parameter ζ, damping α, oblique angle ψ and dc field h_0 depends on the amplitude ξ, here we have $h = \xi/(2\sigma)$ and frequency ω of the ac field.

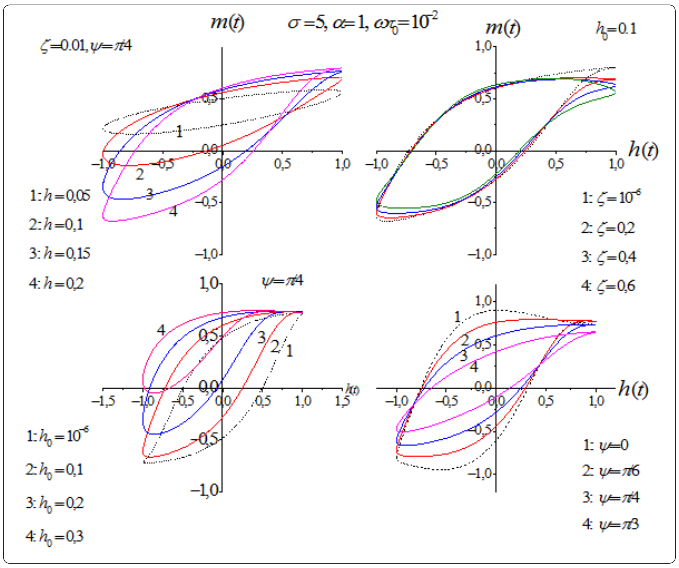

Figure 2: (Color on line) DMH loops for barrier parameter σ = 10, damping α=1, dimensionless frequency $\omega\tau_0 = 10^{-3}$, for various ac magnetic field, various antiferromagnetic parameter ζ, various dc field and various angle.

Figure.3.show, that the shape and area of DMH loops strongly depend the amplitude of the ac magnetic field and the antiferromagnetic at low frequencies, where changes of the ac field are quasi-adiabatic, the magnetization dynamics represent the so-called switching regime meaning that the magnetization may reverse due to the cooperative shuttling action of thermal agitation and applied field.

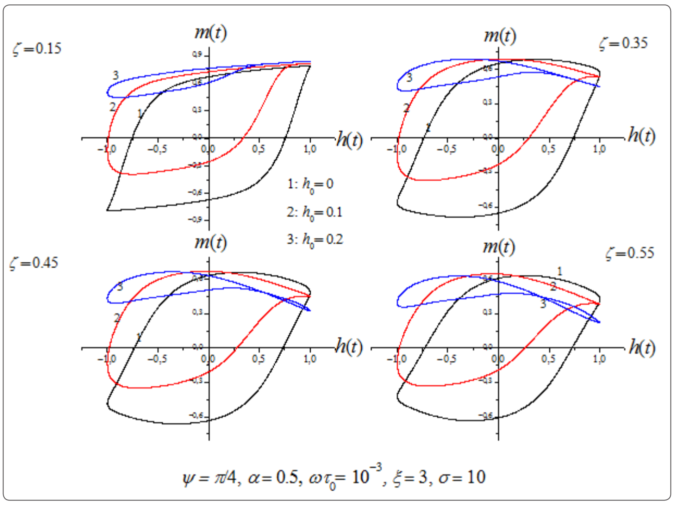

Figure 3: (Color on line) DMH loops for barrier parameter σ = 10, damping α=0.5, ac field parameter ξ=3, dimensionless frequency ωτ0 = 10^{-3}, angle ψ = π/4 and various dc field h_0 = 0, 0.1, 0.2 and various values of the antiferromagnetic parameter ζ.

Now for moderate AC field, and at high frequency, $\omega\tau_0 = 1$, the DMH loops have an ellipsoidal shape (see Figure. 4) so that we may again infer that only a few harmonics actually contribute to the nonlinear response. The DMH loop area decrease substantially. On increasing the barrier, we may perceive a different qualitative behavior of the DMH with oblique angle of the magnetic field. In effect, in this band of frequency range, the field variations compete with thermal agitation. The DMH arising from a high-frequency periodic signal may be evaluated permitting quantitative analysis of ultrafast switching of the magnetization in antiferromagnetic. At

$\omega \sim \omega_{pr}$, DMH occurs due to the resonant behavior of the nonlinear response and under such conditions the switching may be termed "resonant", leading naturally to the concept of resonant switching of the magnetization [19].

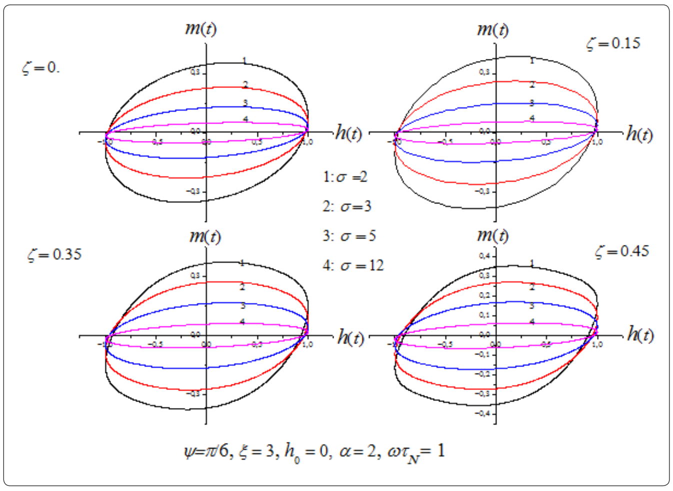

Figure 4: (Color on line) DMH loops for damping α=2, ac field parameter ξ=3, dimensionless frequency $\omega\tau_0$=1 (High Frequency), dc field h_0 = 0 and various value of the barrier parameter.

Figure.5 illustrates The DMH loop area decreases as the antiferromagnetic parameter ζ increases. Moreover, the coercivity, the remanent magnetization, and the saturation magnetization strongly depend on σ, so that considerable variations in the area and shape of loops exist for different values of σ at low frequency.

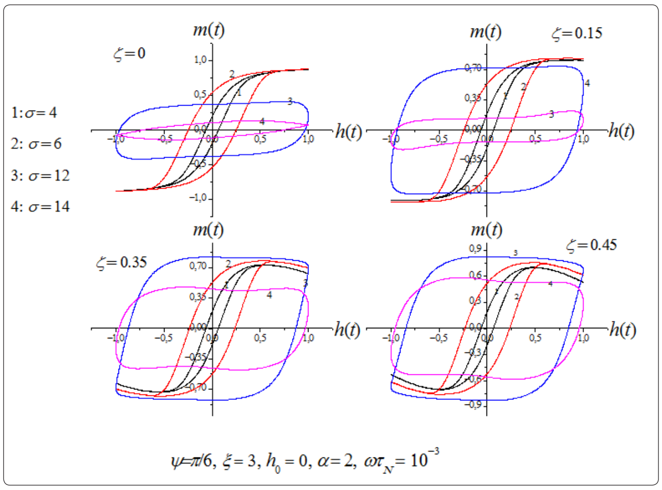

Figure 5: (Color on line) DMH loops for damping α =2, ac field parameter ξ=3, dimensionless frequency $\omega\tau_0$=10^{-3} (Low Frequency), dc field h_0 =0 and various value of the barrier parameter.

Figure. 5 illustrates that the area of the DMH loops decreases with increasing the dc field parameter h_0. Also with decreasing the anisotropy parameter σ, i.e., with increasing temperature, the DMH loops become narrow (Fig. 4a), which implies that a small amount of energy is used up in reversing the magnetization. Figure 4c illustrates the dependence of the shape and area of DMH loops on the oblique angle ψ. While in Fig. 4d, DMH loops are presented for very low and intermediate frequencies. At low frequencies, $\omega\tau_N$ ~10^{-4}-10^{-3} the loops are large while at intermediate frequencies, $\omega\tau_N$ ~ 1, the shape of loops becomes elliptic with small area.

The shape and area of DMH loops alter as the antiferromagnetic parameters ζ varies (see Figs. 4 and 5). In particular, as seen in Fig. 6, A_n strongly depends on temperature, namely, on increasing σ~T^{-1}, i.e., decreasing temperature, the normalized area initially increases, reaches a maximum, and then decreases. Furthermore, at low σ (high temperatures), the behavior of A_n for antiferromagnetic and ferromagnetic nanoparticles is very similar while for large σ >10 it can differ substantially. Figure 6 shows the behavior of the normalized area A_n , Eq. (9), as a function of the ac field ξ for various anisotropy (inverse temperature) parameters σ~T^{-1}. For a weak ac field, the DMH loops are ellipses with normalized area A_n given by Eq. (9); In *strong* ac fields, ξ>1 , the DMH area alters substantially (see Fig. 7); nevertheless, A_n is still determined by -Im (m_1^1) [cf. Eq. (9)] with maxima when the antiferromagnetic parameter is very small.

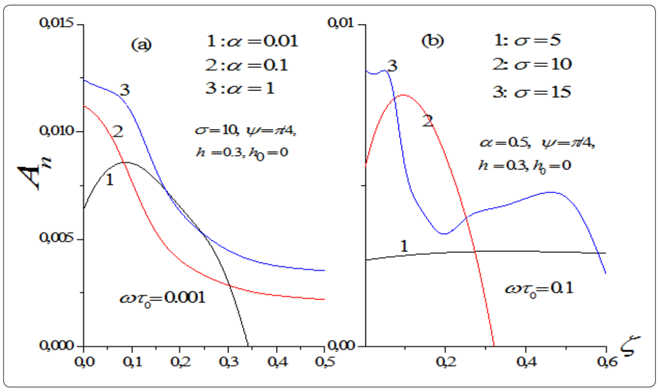

Figure 6: (Color on line) Normalized area A_n of the DMH loop vs. various antiferromagnetic parameters ζ , anisotropy (inverse temperature) parameter σ=10, for the ac field parameter ξ=3, damping α=1, and zero dc field h_0 = 0 (a) frequency: $\omega\tau_N$=10^{-3}, (b) frequency : $\omega\tau_N$=10^{-2}.

Conclusion

Dynamics magnetic Hysteresis of super-antiferromagnetic nanoparticles is studied using Brown's continuous diffusion model as adapted to antiferromagnetic nanoparticles by Raikher and Stepanov [8]. The calculations of the DMH loops have been carried out by means of the effective matrix continued-fraction method originally developed for ferromagnetic nanoparticles [18] showing a marked dependence of these quantities on the specific antiferromagnetic parameter ζ. It is found that under appropriate conditions a small (in comparison with that of internal anisotropy) bias dc field can strongly affect the shape of DMH loops in antiferromagnetic nanoparticles. This result implies that varying the dc bias field strength, one may effectively control the heat production (specific power loss) in a nanoparticle. Since the results are valid for ac fields of *arbitrary* strength and orientation, they provide a rigorous basis for treatment of the nonlinear ac stationary response of antiferromagnetic nanoparticles in a strong ac fields, where perturbation theory is no longer valid. Our calculations of the nonlinear response of an individual antiferromagnetic nanoparticle can be generalized to calculate the average magnetic moment of an assembly of randomly oriented noninteracting uniaxial particles by averaging over particle easy axis orientations as described in detail in Ref. [19].

Acknowledgments

We thank W. T. Coffey and Kalmykov for a critical reading of the paper and useful comments and suggestions.

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