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Magneto-orientational behavior of a suspension of antiferromagnetic particles

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Abstract

A theory describing magneto-orientational properties of suspensions containing antiferromagnetic nanoparticles is developed. Due to their small size, these particles possess, apart from an anisotropic magnetic susceptibility pertinent to antiferromagnets, a spontaneous magnetic moment caused by sublattice decompensation. In a colloid subjected to a DC field of increasing strength an orientational crossover takes place: the particle magnetic moments, initially aligned along the field, turn to the transverse orientation. This behavior considerably changes the observable characteristics of the system: the spectrum of linear dynamic susceptibility and the integral time of magnetic relaxation under a pulse field.

1. Introduction

Recently, multidisciplinary interest in the properties of dispersions based on antiferromagnetic nanoparticles has grown rapidly. The most well-known example is ferritin, both as a natural colloid involved in some intracellular processes in living beings [1, 2] and as an artificial size-calibrated nanograin medium for applications [3]. A less well-known issue is that of nanogranular ferrihydrite synthesized by certain pelobiont bacteria [4]. In contrast with customary magnetic fluids, whose physics is well developed, antiferromagnetic colloids display some new and not fully understood features. In particular, this concerns their magnetodynamical properties.

Specific behavior of single-domain antiferromagnetic grains was predicted in the pioneering works of Néel [5]. The main concept is based on the fact that in a fine particle, where the number of spins is quite limited, the magnetic compensation of the sublattices is incomplete, yielding a spontaneous (decompensation) magnetic moment μ . Néel estimated its magnitude from simple statistical considerations; for a quasi-spherical fine grain he obtained $\mu \sim \mu_B z N^{1/2}$, where z is the number of spins per atom, μ_B the Bohr magneton, N the number of magnetic atoms in the particle. For a nanoparticle (~ 10 nm) the number N ranges over 10^5 – 10^6 . This means that the magnetic moment of such an object is about 0.1–1% of that of a ferromagnetic one. Taking 300 G as a reference value, one finds that the effective spontaneous magnetization of a nanosize antiferromagnetic (NAF) particle

is about or less than one gauss, which is a small but by no means negligible value.

Denoting the sublattice net magnetic moments of a nanoparticle by μ_1 and μ_2 , with allowance for decompensation we write their absolute values as

$$\mu_1 = I_s V + \frac{1}{2}\mu, \quad \mu_2 = I_s V - \frac{1}{2}\mu, \quad (1)$$

where I_s is the reference bulk value of the sublattice magnetization and V the particle volume. In the temperature range below the Néel point we set the decompensation magnetic moment μ constant and assume equation (1) to be valid for applied fields lower than the exchange one. In this limit the antiferromagnetic vector defined as $e = (\mu_1 - \mu_2)/2I_s V$ may rotate but cannot change its length. In a NAF particle it defines also the direction of the decompensation magnetic moment $\boldsymbol{\mu} = \mu e$.

A specific feature of any antiferromagnet is a considerable magnetic susceptibility χ_A in the direction across the antiferromagnetic vector. This response mechanism is due to the ‘elastic tilt’ of sublattices under an external field. According to Néel [6], in fine particles the value of χ_A is enhanced up two times against the corresponding value pertinent to a bulk crystal due to a specific superantiferromagnetic effect. In our model we describe the field-induced magnetic moment of a NAF particle using the linear susceptibility tensor

$$\chi_{ik} = \chi_A (\delta_{ik} - e_i e_k), \quad (2)$$

where χ_A is an effective value. Tensor χ_{ik} is defined for a unit volume of the particle; its component in the direction of e is zero. Expressing the sublattice magnetic moments with the aid of equations (1) and (2), one gets

$$\mu_{1,2} = \pm(I_s V \pm \frac{1}{2}\mu)e - \chi_A V(eH)e. \quad (3)$$

In terms of equation (3), the Zeeman energy of a particle takes the form

$$U_H = -\mu(eH) + \frac{1}{2}\chi_A V(eH)^2; \quad (4)$$

the coefficient $\frac{1}{2}$ in the last term is due, as usual, to integration over the field strength.

The particle magnetic anisotropy is taken to be uniaxial with K being the corresponding energy density and n a unit vector of the easy axis. Then the anisotropy energy is written as $U_A = -KV(en)^2$, which in combination with equation (4) yields the expression for the energy of a NAF particle:

$$U = -\mu(eH) + \frac{1}{2}\chi_A V(eH)^2 - KV(en)^2. \quad (5)$$

This formula closely resembles the one used for phenomenological description of a single-domain ferromagnetic particle. In particular, the magnetic state of a NAF grain is determined by the same pair of variables: the unit vector of the permanent magnetic moment e and the easy-axis vector n . However, at present equation (5) incorporates two, not one, Zeeman terms which imply competing equilibrium orientations of the particles with respect to the applied field. Indeed, as seen from equation (5), in a static field $H < \mu/\chi_A V$ the particle aligns its axis n parallel to H while at $H > \mu/\chi_A V$ the axis is tilted with respect to the field direction, the tilt angle growing gradually to 90° . This means that in a NAF colloid at $H_* = \mu/\chi_A V$ an orientational crossover takes place: the equilibrium axes distribution, being of the easy-axis type at $H < H_*$, turns into a ‘cone phase’ at $H > H_*$ and tends to the easy-plane one at $H \gg H_*$.

Quantitative differences between NAF and ferromagnetic cases are also important. Note that due to the decompensation origin of the magnetic moment the ratio

$$\xi = \mu H/kT \quad (6)$$

for NAF grains of a size ~ 10 nm is two orders of magnitude smaller than that for the same ferromagnetic particles. Meanwhile the parameter

$$\sigma = KV/kT, \quad (7)$$

that determines the probability of thermofluctuational magnetic inversion (superparamagnetism) remains the same. To this set one should add the parameter

$$\varkappa = \frac{1}{2}\chi_A V H^2/kT, \quad (8)$$

non-existent for ferromagnetic particles.

2. Static properties

In what follows we develop a theory of magnetic properties of NAF suspensions (colloids) as a modification of the approach used for dilute magnetic fluids (MF), i.e., a model of a gas

of non-interacting magnetic dipoles. In this connection one fact of fundamental significance should be remarked. Since the magnetodipole interaction is proportional to the square of the particle magnetic moment, in NAF colloids this factor is at least four orders of magnitude lower than in MF. This means that for NAF systems the ‘dilute’ description is well applicable for any colloid concentration.

The observed magnetic moment of a particle is defined in a standard way as a derivative of its free energy with respect to the field: $m = -\partial F/\partial H$. In an assembly of non-interacting particles at temperature T one has

$$m_i = \mu\langle e_i \rangle_0 + \chi_A V(\delta_{ik} - \langle e_i e_k \rangle_0)H_k, \quad (9)$$

where angular brackets denote averaging with the equilibrium distribution function $W_0 \propto \exp(-U/kT)$. In general, m depends on the above-introduced parameters (6)–(8) and on the angle between the field and the particle axis. For both liquid and solid NAF dispersions a convenient way to evaluate m is provided by the matrix sweep method described in [7], for example. At small ξ , i.e., in a field of weak to moderate strength, the result could be found analytically. In particular, for a solid dispersion with random axes distribution one gets

$$m = \frac{1}{3}\mu\xi[1 - \frac{1}{15}\xi^2(1 + 2S_2) - \frac{4}{15}\varkappa(1 - S_2)] + \frac{2}{3}\chi_A V H[1 - \frac{2}{15}(\xi^2/2 - \varkappa)(1 - S_2)]. \quad (10)$$

Here the order parameter $S_2 = \langle P_2(en) \rangle_0$, with P_2 being the second Legendre polynomial, describes the orientation of vector e with respect to the particle anisotropy axis. Since variation of P_2 is limited, function $S_2(\sigma)$ varies from zero (magnetoisotropic) to unity (magnetically hard particles). Substituting $S_2 = 0$ in equation (10) one recovers the classical result [5] since in Néel’s studies magnetic anisotropy was neglected.

Meanwhile, the anisotropy constant K in antiferromagnets could be substantial, e.g. in ferritin it is several times 10^5 erg cm^{-3} . As seen from equation (10), for strong anisotropy ($\sigma \gg 1$, $S_2 \sim 1$) the moment m depends only on the parameter ξ for an arbitrary value of the latter. Indeed, at strong anisotropy one may pass to a simple two-level (Ising) approximation that yields the magnetic moment in the form

$$m = \chi_A V(1 - \cos^2 \psi) + \mu \cos \tanh(\xi \cos \psi), \quad (11)$$

where ψ is the angle between the easy axis and the field direction. For random orientation, integrating equation (11), one gets [8]

$$m = \frac{2}{3}\chi_A V H + \mu G(\xi), \quad G(\xi) = \int_0^1 y \tanh(\xi y) dy. \quad (12)$$

In NAF colloids the nanograins are free to rotate. We ascribe them a strong (infinite) magnetic anisotropy and set $e = n$, thus adopting a ‘rigid-dipole’ approximation. In this case the energy function formally coincides with equation (4). After averaging over the equilibrium state, for the colloid magnetization one obtains

$$M = cm = c\mu\{\langle P_1(x) \rangle_0 + \frac{2}{3}q[1 - \langle P_2(x) \rangle_0]\}. \quad (13)$$

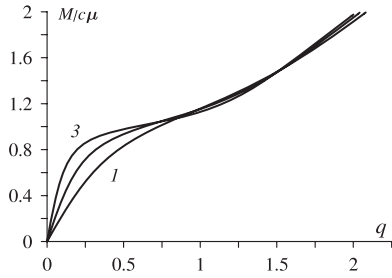


Figure 1. Reduced static magnetization of a NAF colloid.

where c is the particle number concentration, $\mathbf{h} = \mathbf{H}/H$ a unit vector of the external field, $x = (\mathbf{e}\mathbf{h})$ and $q = H/H_*$ the dimensionless field strength. At $q \ll 1$ the averages of P_1 and P_2 are close to the corresponding Langevin functions of argument $\xi = \beta q$, where $\beta = \mu H_*/kT$ is hereafter used as a dimensionless temperature parameter. At $q \sim 1$ (around the crossover) these functions reach maxima and at $q > 1$, due to the negative contribution of the term $\kappa = 1/2\beta q^2$, decrease, tending to 0 and $-1/2$, respectively. Meanwhile, the magnetization grows unboundedly due to the linear term in equation (13). This behavior is shown in figure 1, where the lines correspond to $\beta = 5(1), 10$ and $20(3)$.

3. Dynamics of magnetization

To build a description of magnetodynamics for NAF colloids in the same ‘rigid-dipole’ limit, we start with the conventional kinetic Fokker–Planck equation [7]:

$$2\tau \partial W / \partial t = \mathbf{J}W\mathbf{J}(U/kT + \ln W); \quad (14)$$

here τ is the time of rotary diffusion of a particle in a liquid matrix and $\mathbf{J} = (\mathbf{e} \times \partial/\partial \mathbf{e})$ an infinitesimal rotation operator. The orientation distribution function is expanded in a series of spherical harmonics

$$W(\mathbf{e}, \mathbf{h}, t) = \sum_{l=1}^{\infty} \sum_{k=-l}^{k=l} b_{lk}(t) \frac{2l+1}{4\pi} \frac{(l-|k|)!}{(l+|k|)!} X_l^{k*}(\mathbf{e}\mathbf{h}), \quad (15)$$

where $X_l^k = P_l^k(\cos \vartheta)e^{ik\varphi}$ are expressed in terms of angular coordinates in a spherical framework with the polar axis along \mathbf{h} ; P_l^k are associated Legendre polynomials. In representation (15) the dynamics of the system is determined by the coefficients $b_{lk}(t) = \langle X_l^k \rangle$ which obey a chain-like set derived from equation (15):

$$\begin{aligned} 2\tau \frac{db_{lk}}{dt} + l(l+1)b_{lk} + \beta q^2 \left[\frac{(l+1)(l+k-1)(l+k)}{(2l-1)(2l+1)} b_{l-2,k} \right. \\ \left. + \frac{l(l+1) - 3k^2}{(2l-1)(2l+3)} b_{lk} - \frac{l(l-k+2)(l-k+1)}{(2l+1)(2l+3)} b_{l+2,k} \right] \\ - \frac{\beta q}{2l+1} [(l+1)(l+k) b_{l-1,k} - l(l-k+1) b_{l+1,k}] \\ = 0. \end{aligned} \quad (16)$$

To find a response of a NAF colloid to a dynamic probing, we add to the particle energy (4) a term $U_1 = -\mathbf{e}\mathbf{H}_1(t)$, where a

weak AC (probing) field changes harmonically:

$$\mathbf{H}_1(t) = \frac{1}{2} H_{10} (e^{i\omega t} + e^{-i\omega t}) \mathbf{h}_1, \quad |\mathbf{h}_1| = 1. \quad (17)$$

If this is the only field imposed, the linear susceptibility calculation is easy and yields

$$\chi(\omega) = \frac{c\mu^2}{3kT} \frac{1}{1+i\omega\tau} + \frac{2cV}{3} \chi_A. \quad (18)$$

If besides the probing one, a static magnetizing field \mathbf{H} is present, the macroscopic magnetic susceptibility is anisotropic. From equations (15) and (16) it follows that the components of the perturbed magnetization parallel and normal to the field are

$$\begin{aligned} \delta M_{\parallel} &= c\mu [b_{10}(\omega) - \frac{2}{3} b_{20}(\omega)] \\ &+ \frac{2}{3} c\chi_A V [1 - \langle P_2(\mathbf{e}\mathbf{h}) \rangle_0] H_1, \\ \delta M_{\perp} &= c\mu [b_{11}(\omega) - \frac{1}{3} b_{21}(\omega)] \\ &+ \frac{1}{3} c\chi_A V [2 + \langle P_2(\mathbf{e}\mathbf{h}) \rangle_0] H_1. \end{aligned} \quad (19)$$

Here the moments b_{lk} of the non-equilibrium distribution function are obtained by solving anew the set (16) where now the rhs of the lines (l, 0) and (l, 1) are $\beta q_1 f_{l0}$ and $\beta q_1 f_{l1}$, with functions f depending on l, q and the equilibrium averages $\langle P_l(\mathbf{e}\mathbf{h}) \rangle_0$.

The paramagnetic susceptibility of NAF particles adds to formulas (19) the frequency-independent contributions. At $H = 0$ the system has no pre-orientation, $\langle P_l(\mathbf{e}\mathbf{h}) \rangle_0 = 0$ and the two lines of equation (19) coincide. Under strong fields, where $\langle P_l(\mathbf{e}\mathbf{h}) \rangle_0 = 1$, the perpendicular term is maximal while the parallel one turns to zero. As the frequency range in question lies far below that of electron spin resonance at given H , the corresponding susceptibilities may be written as

$$\chi_{\infty}^{(\parallel)} = \delta M_{\parallel}(\omega \rightarrow \infty)/H_1, \quad \chi_{\infty}^{(\perp)} = \delta M_{\perp}(\omega \rightarrow \infty)/H_1. \quad (20)$$

4. Dynamic susceptibility under magnetizing field

In the theory of linear susceptibility in dilute magnetic fluids [9] the pertinent function $\chi(\omega, H)$ is given by the Debye factor $[1 - i\omega\tau_{\alpha}(H)]^{-1}$, where $\tau_{\alpha}(H)$ is a known function and the subscript α is either \parallel or \perp . In a NAF colloid the situation is more complicated due to the orientation crossover occurring at $H = H_*$. From equation (4) it follows that below the crossover ($q < 1$) the equilibrium orientation state of the colloid is of the easy-axis type, and both components of the susceptibility, χ_{\parallel} and χ_{\perp} , closely resemble that of an ordinary MF. This means that the magnetization relaxation is dominated by the most long-living eigenmode of equation (16) which further on we shall term the dipole mode.

Starting at the crossover point $q = 1$ and on further increase of the magnetizing field, the basic state of the colloid, according to equation (4), tends to an easy-plane structure defined by unit vector \mathbf{h} . There the decisive contribution to the relaxation process is rendered by the second (quadrupole) mode of equation (16). A full multimode analysis of this equation proves that the joint contribution of all the higher

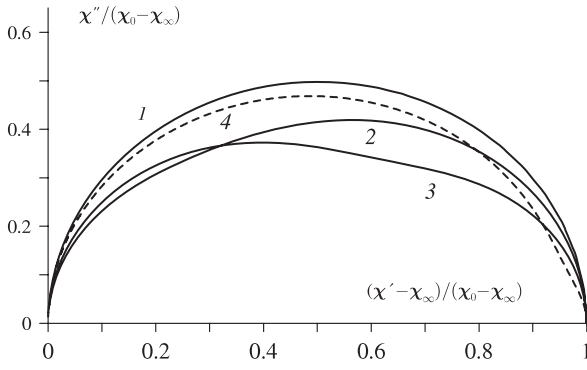


Figure 2. Cole–Cole diagrams for transverse magnetic susceptibility of a NAF colloid at $\beta = 6$ in the magnetizing field $q = 0.5(1)$, $1.1(2)$, $1.4(3)$, $2.0(4)$; here $\chi_0 = \chi^{(L)}(\omega = 0)$.

eigenmodes is always low. However, the ‘participations’ of quadrupole modes in longitudinal and transverse relaxations are qualitatively different. For the longitudinal case the effect manifests itself only in the vicinity of the crossover point. There the dipole mode virtually disappears, and the quadrupole one rules the process. This type of mode mixing does not affect much the corresponding dynamic susceptibility $\chi_{\parallel}(\omega, q)$, but reflects itself strongly under pulse fields, as shown below in section 5.

In the transverse magnetic relaxation the weight of the quadrupole mode increases monotonically with q at the expense of that of the dipole one. This effect is not very significant for pulse probing but strongly affects the dynamic susceptibility. To facilitate both theoretical illustration and experimental verification of the phenomenon, we present it in terms of Cole–Cole diagrams. For that, one subtracts from the transverse complex susceptibility its frequency-independent part and plots a normalized imaginary part $|\chi''(\omega)|$ as a function of the real one $\chi'(\omega)$. The result is shown in figure 2. As seen, in a weak field ($q < 1$) the diagram is very close to the Debye half-round (curve 1) characteristic of oscillation of a single dipole mode. For the crossover conditions, where the spectrum essentially incorporates both modes, the curve becomes more complicated. We note that if the difference between the reference times were large, the diagram would have split into two separate half-rounds. In the system under study, due to the proximity of the reference times ($\tau^{\text{quad}} \approx \tau^{\text{dip}}/3$) this splitting does not resolve completely but yields a considerable flattening of the diagram; see curves 2 and 3. On

further increase of the field strength, a simple Debye shape is restored (line 4), which means a regime for a single quadrupole mode. In other words, far from the crossover the magnetization relaxation is a single-mode process, while around $q = 1$ it is essentially bimodal.

5. Integral relaxation times

Pulse fields provide another way to both probe magnetic properties of colloids and control their magneto-orientational behavior. A convenient way to characterize a multimode response to a pulse excitation is via the *integral relaxation time* (IRT). It is evaluated by dividing the time integral of the response function taken over the interval $[0, \infty]$ by the initial value of this function. For example, IRT for magnetization is written as

$$\tau^* = [\delta M(0)]^{-1} \int_0^{\infty} \delta M(t) dt.$$

An important merit of IRT is that it incorporates contributions from all the modes and thus helps to reveal the multimode nature of the longitudinal magnetization mentioned in section 4. Evaluating the first two (main) ‘longitudinal’ ($k = 0$) eigenvalues from the set (16), one obtains the relaxation times for these modes. As functions of the field strength they both decrease with q , being bounded by the limiting values

$$\tau_{\parallel}^{\text{dip}} = \tau \begin{cases} 1, & \text{at } q = 0, \\ 0, & \text{at } q \rightarrow \infty; \end{cases}$$

$$\tau_{\parallel}^{\text{quad}} = \tau \begin{cases} \frac{1}{3}, & \text{at } q = 0, \\ 0, & \text{at } q \rightarrow \infty. \end{cases}$$

In figure 3 the actual behavior of these partial relaxation times is shown by dashed lines. We recall that in the longitudinal magnetic response the weights of the dipole and quadrupole modes change non-monotonically with q . The dipole mode dominates on both sides of the crossover but turns to zero at $q \sim 1$. Due to that, in this region IRT deviates strongly from the line $\tau_{\parallel}^{\text{dip}}(q)$ and virtually coincides with the function $\tau_{\parallel}^{\text{quad}}(q)$. At $\beta > 1$, function $\tau_{\parallel}^*(q)$ has a minimum located in the crossover region; see figures 3(b) and (c).

IRT for the transverse ($\mathbf{H}_1 \perp \mathbf{H}$) pulse magnetization of a NAF colloid is also non-trivial due to a combination of two facts. First, the mode weights change gradually from the dipole

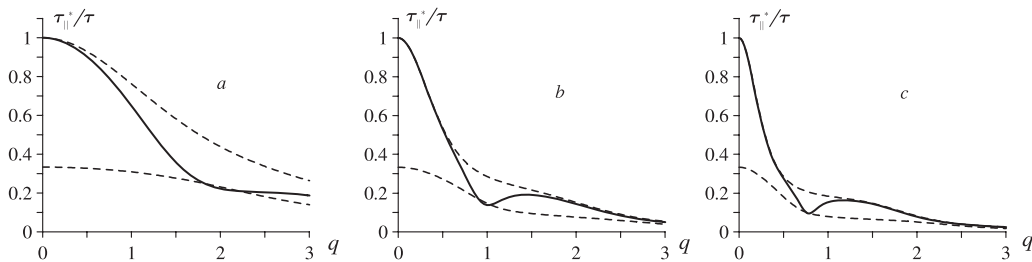


Figure 3. Solid lines: longitudinal integral relaxation time for a NAF colloid at $\beta = 1$ (a), 5 (b) and 10 (c); dashed lines: relaxation times for decoupled dipole and quadrupole modes.

at $q \ll 1$ to the quadrupole mode at $q \gg 1$. Second, the partial times behave in a specific way:

$$\tau_{\perp}^{\text{dip}} = \tau \begin{cases} 1, & \text{at } q = 0, \\ 2, & \text{at } q \rightarrow \infty; \end{cases}$$

$$\tau_{\perp}^{\text{quad}} = \tau \begin{cases} \frac{1}{3}, & \text{at } q = 0, \\ 0, & \text{at } q \rightarrow \infty. \end{cases}$$

As a result, $\tau_{\perp}^*(q)$ goes down monotonically but the slope of this curve oscillates. Note that in the transverse case the dipole time never turns to the ‘dynamic’ limit ($\propto \tau/\xi$) and always remains temperature dependent. Accordingly, in the region $q \gg 1$ it is completely ‘expelled’ from IRT.

6. Conclusions

A model is proposed that describes low frequency magnetodynamic behavior of nanosuspensions (colloids) of fine antiferromagnetic grains; the latter are assumed to possess anisotropic susceptibility and a permanent (decompensation) magnetic moment. We show that the dynamic susceptibility and pulse field response characteristics (the Cole–Cole plots, in particular) display certain features which strongly distinguish NAF colloids from usual magnetic fluids.

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