Nonlinear susceptibility of superparamagnets with a general anisotropy energy

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The equilibrium nonlinear response of noninteracting superparamagnets with a general single-spin anisotropy is investigated. Generalizing the results obtained for the simplest uniaxial anisotropy [García-Palacios and Lázaro, Phys. Rev. B **55**, 1006 (1997)], we derive a formula for the nonlinear susceptibility of spin ensembles with randomly distributed anisotropy axes, $\bar{\chi}^{(3)}$, valid for *any* magnetic anisotropy with inversion symmetry. The analysis of this expression reveals that: (i) $\bar{\chi}^{(3)}$ is always negative, (ii) unlike the linear susceptibility, $\bar{\chi}^{(3)}$ remains anisotropy dependent after the random axes average (except for cubic anisotropy, for which $\bar{\chi}^{(3)}$ is equal to that of isotropic spins), (iii) the anisotropy always increases the magnitude of the nonlinear response, and (iv) since this increase depends on temperature, $\bar{\chi}^{(3)}$ deviates from the common $\bar{\chi}^{(3)} \propto T^{-3}$ laws. The general expression for $\bar{\chi}^{(3)}$ is finally particularized to superparamagnets with competing uniaxial and cubic anisotropies and superparamagnets with biaxial anisotropy (arbitrary "shape" anisotropy), for which we study the crossovers between the different regimes (isotropic, discrete orientation, and plane rotator) induced by the magnetic anisotropy.

I. INTRODUCTION

The study of classical spin systems has shed much light on the properties of their quantum counterparts and constitutes, in addition, an important field of research in its own right. Besides, there exist certain systems for which a description in terms of classical spins captures the essential physics in certain ranges, for instance, molecular magnetic clusters with high spin in their ground state ($S \sim 10$) and magnetic nanoparticles ($S \sim 10^2 - 10^5$); both systems will here be referred to as *superparamagnets*. Although we use the language of magnetism, we could also include here systems as the so-called *relaxor ferroelectrics*, in which the net polarization of small polar regions can reorient due to thermal activation between several equienergetical orientations, leading to a *superparaelectric* behavior.

Among the various experimental realizations of superparamagnets, some approximately consist of noninteracting entities. The understanding of the properties of classical, noninteracting systems is besides very important for the subsequent study of their quantum, interacting counterparts. For example, owing to an insufficient knowledge about some properties of independent superparamagnets, it is not always known from which "laws" the associated quantities depart as a consequence of interspin interactions. Similar considerations also apply to the study of quantum phenomena in these systems; as complete a knowledge as possible of the classical regime is a prerequisite for the study of, for instance, quantum tunneling and coherence.

A. Magnetic anisotropy and extent of the equilibrium (superparamagnetic) range

The single-spin anisotropy plays a fundamental role in the behavior of superparamagnets. Nevertheless, the effects of the anisotropy on the *thermal-equilibrium* properties of these systems are sometimes overlooked because superparamagnetism is *restrictively* ascribed to the temperature range in which the heights of the energy barriers (created by the magnetic anisotropy) are lower than the thermal energy. Let us briefly show the limitations of this view.

In the moderate-to-high barrier range, the characteristic time τ for the rotation of a classical spin \vec{m} over the energy barrier ΔU can be written in the Arrhenius form

$$\tau = \tau_0 \exp(\beta \Delta U), \tag{1.1}$$

where $\beta = 1/k_{\rm B}T$ and the pre-exponential term is weakly dependent on temperature $(\tau_0 \sim 10^{-7} - 10^{-8} \text{ s}$ for molecular magnetic clusters and $\tau_0 \sim 10^{-10} - 10^{-12} \text{ s}$ for magnetic nanoparticles). Then, for a given measurement time $t_{\rm m}$, the spins display their thermal-equilibrium response when the condition of superparamagnetism, $\tau \ll t_{\rm m}$, is obeyed, which corresponds to the temperature range:

$$\ln(t_{\rm m}/\tau_0) > \beta \Delta U \ge 0. \tag{1.2}$$

For instance, for "static" measurements $(t_m \sim 1-100 \text{ s})$ this range is extremely wide $(25 > \beta \Delta U \ge 0)$, showing that the mentioned ascription of superparamagnetism to the range in which the thermal energy is larger than the anisotropy barriers $(1 \ge \beta \Delta U \ge 0)$ is unduly restrictive.

The preceding considerations also entail that, without leaving the superparamagnetic regime, there are ranges in which $\beta \Delta U \ll 1$ (isotropic behavior), $\beta \Delta U \sim 1$ (intermediate behavior), or $\beta \Delta U \gg 1$ (discrete-orientation behavior). Thus, common approaches such as the isotropic or the discrete-orientation ones have a restricted range of validity for themselves, while, even with the combined use of both, the effects of the *crossover* between the different ranges are lost.

B. Linear and nonlinear responses

One of the most informative tools to investigate the properties of spin systems is the analysis of its linear response. This analysis could give, for instance, important information about the symmetry and strength of the magnetic anisotropy

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in superparamagnets. A simple calculation shows, however, that the linear susceptibility of an ensemble of noninteracting classical dipole moments with a general anisotropy energy [simply obeying $\mathcal{H}(\vec{m}) = \mathcal{H}(-\vec{m})$], is *completely independent* of the anisotropy if the orientations of the anisotropy axes are *distributed at random*.

The analysis of the nonlinear response can then be an alternative. The nonlinear susceptibility $\chi^{(3)}$ of superparamagnets with the simplest axially symmetric anisotropy, $\mathcal{H} = -\Delta U(m_z/m)^2$, has recently been theoretically studied.^{1,2} For anisotropy axes distributed at random, $\chi^{(3)}$ can be written in the following two equivalent forms

$$\overline{\chi}_{\text{uni}}^{(3)} = -\frac{1}{30}\beta^3 m^4 [1 - 2\langle z^2 \rangle + 3\langle z^2 \rangle^2]$$

= $-\frac{1}{45}\beta^3 m^4 (1 + 2S_2^2),$ (1.3)

where the overbar denotes average over axes orientations, $z = m_z/m$, and $S_2 = (3\langle z^2 \rangle - 1)/2$ is the *thermal-equilibrium* average of the second Legendre polynomial. (In Ref. 1 the notation $G \equiv \langle z^2 \rangle$ was used, while $\chi^{(3)}$ was expressed compactly in terms of S_2 by the authors of Ref. 2.) It was found that, since the magnetic anisotropy renders $\langle z^2 \rangle$ temperature dependent, $|\chi^{(3)}|$ increases with decreasing temperature *faster* than the common $|\chi^{(3)}| \propto \beta^3$ law. That temperature dependence might mix with other non- β^3 behaviors, such as those associated with interspin interactions, so masking the effect of the latter.¹

We finally mention that, due to both the challenges raised by the recent experiments on individual magnetic nanoparticles³ and by its intrinsic theoretical interest, the pioneering studies of the 1970s on classical spin systems with nonaxially symmetric Hamiltonians are currently being extended (see, for instance, Refs. 4–8). In this context, it would be interesting to generalize the previous work on the nonlinear response of uniaxial spins^{1,2} to other forms of the magnetic anisotropy. In this article we shall give a step toward this objective, by investigating the *equilibrium* nonlinear response of superparamagnets with a *general* single-spin anisotropy.

II. LINEAR AND NONLINEAR SUSCEPTIBILITIES OF SPINS WITH INVERSION SYMMETRY

In this section we derive the susceptibilities of spins whose Hamiltonians have *inversion symmetry* $[\mathcal{H}(\vec{m})] = \mathcal{H}(-\vec{m})]$. To this end, we particularize the expressions given in Appendix A for the linear (χ) and first nonlinear ($\chi^{(2)}$ and $\chi^{(3)}$) susceptibilities in terms of thermalequilibrium averages of the unperturbed spins.

A. Tensor elements

The general formulas of Appendix A simplify notably when the Hamiltonian of the spin has inversion symmetry, since the thermal-equilibrium average of products of an *odd* number of spin components vanishes $(\langle m_{i_1} \cdots m_{i_{2n+1}} \rangle = 0)$. Accordingly, the expressions for the tensor elements of the susceptibilities reduce in this case to

$$\chi_{ii} = \beta \langle m_i m_i \rangle, \qquad (2.1)$$

$$\chi_{ijkl}^{(3)} = \frac{1}{6} \beta^3 [\langle m_i m_j m_k m_l \rangle - \langle m_i m_j \rangle \langle m_k m_l \rangle - \langle m_i m_k \rangle \langle m_i m_l \rangle - \langle m_i m_k \rangle \langle m_i m_l \rangle], \qquad (2.2)$$

while $\chi_{ijk}^{(2)}$ vanishes.

As the condition of inversion symmetry breaks down in the presence of a *bias* field, this case is excluded from our considerations (cf. Ref. 9). It should be remarked, however, that $\mathcal{H}(\vec{m}) = \mathcal{H}(-\vec{m})$ is obeyed by any single-spin anisotropy as a direct consequence of the time-reversal symmetry of the Hamiltonian.¹⁰

B. Effective susceptibilities of spin systems with randomly distributed anisotropy axes

The effective susceptibilities are defined as the coefficients in the expansion in powers of the probing field \vec{b} of the projection of the spin response onto the direction of \vec{b} [see Eq. (A3)]. For an ensemble of *identical* spins with a given distribution of anisotropy axes orientations, these susceptibilities can be obtained by considering one spin and averaging over the corresponding orientations of the probing field $\vec{b}/b = (\alpha_x, \alpha_y, \alpha_z)$. For anisotropy axes distributed at random, this averaging (denoted by a bar) can be performed by means of the following formulas (see, for example, Ref. 11, p. 64)

$$\alpha_i \alpha_j = \frac{1}{3} \,\delta_{ij} \,, \tag{2.3}$$

$$\alpha_i \alpha_j \alpha_k \alpha_l = \frac{1}{15} (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}), \qquad (2.4)$$

where δ_{ij} is the Kronecker delta. Ensembles of nonidentical spins can be handled analogously, by first averaging over subsets of identical spins with help from these expressions, and then summing the results obtained over the different subsets (for instance, integrating over the size and shape distributions in nanoparticle ensembles).

1. Effective linear susceptibility

The effective linear susceptibility [Eq. (A4)] of an ensemble of spins with randomly distributed anisotropy axes is given by

$$\bar{\chi} \equiv \sum_{ij} \chi_{ij} \overline{\alpha_i \alpha_j} = \frac{1}{3} \sum_i \chi_{ii},$$

which is essentially the trace of the susceptibility tensor. Then, on using the expression (2.1) for spins with inversion symmetry and taking advantage of the commutative character of the summation and the averaging, one finds $\bar{\chi} = (\beta/3) \sum_i \langle m_i^2 \rangle = (\beta/3) \langle \sum_i m_i^2 \rangle$. However, the quantity inside the last average symbol is a constant equal to m^2 , so one finally obtains the simple result

$$\bar{\chi} = \frac{1}{3}\beta m^2. \tag{2.5}$$

Note that, after the random axes average, all vestiges of the magnetic anisotropy disappear from the linear susceptibility, irrespective of the *symmetry* or *magnitude* of the anisotropy terms. Our next goal is to determine to which extent a result with this generality can be established for the nonlinear response.

2. Effective nonlinear susceptibility

Proceeding analogously from Eq. (A5) for $\chi^{(3)}$ and using Eq. (2.3) we first obtain

$$\bar{\chi}^{(3)} \equiv \sum_{ijkl} \chi^{(3)}_{ijkl} \overline{\alpha_i \alpha_j \alpha_k \alpha_l} = \frac{1}{5} \sum_{ij} \chi^{(3)}_{iijj},$$

where we have taken into account $\chi_{iijj}^{(3)} = \chi_{ijjj}^{(3)} = \chi_{ijji}^{(3)}$ [see the definition (A2)]. From Eq. (2.2) for systems with inversion symmetry, we get for the tensor element required the following expression:

$$\chi_{iijj}^{(3)} = \frac{1}{6}\beta^3 [\langle m_i^2 m_j^2 \rangle - \langle m_i^2 \rangle \langle m_j^2 \rangle - 2 \langle m_i m_j \rangle^2].$$

Then, interchanging again summations and averages, one can see that the first two terms on the right-hand side of this formula cancel each other upon summing over i (or j). Consequently, one is left with the following expression for the effective nonlinear susceptibility of an ensemble of spins with randomly distributed anisotropy axes

$$\bar{\chi}^{(3)} = -\frac{1}{15}\beta^3 \sum_{ij} \langle m_i m_j \rangle^2.$$
 (2.6)

3. Alternative expression for the effective nonlinear susceptibility

Let us now cast Eq. (2.6) into a form that proves to be particularly convenient for both its interpretation and computation. First, if we choose the coordinate system in which $\langle m_i m_j \rangle$ is diagonal (the same system that diagonalizes the susceptibility tensor χ_{ij}), we have $\bar{\chi}^{(3)} =$ $-(1/15)\beta^3 \Sigma_i \langle m_i^2 \rangle^2$. Then, if we introduce the components of the normalized magnetic moment, namely, $x = m_x/m$, $y = m_y/m$, and $z = m_z/m$, as well as the quantities

$$S_2 = \frac{1}{2} (3\langle z^2 \rangle - 1), \quad \Delta = \frac{1}{2} (\langle y^2 \rangle - \langle x^2 \rangle), \quad (2.7)$$

the second-order moments required can be written as

$$\langle x^2\rangle = \frac{1-S_2}{3} - \Delta, \quad \langle y^2\rangle = \frac{1-S_2}{3} + \Delta, \quad \langle z^2\rangle = \frac{1+2S_2}{3} + \Delta,$$

Finally, on squaring and adding the right-hand sides of these expressions and introducing the result obtained in $\bar{\chi}^{(3)} = -(1/15)\beta^3 \Sigma_i \langle m_i^2 \rangle^2$, we arrive at the formula

$$\bar{\chi}^{(3)} = -\frac{1}{45}\beta^3 m^4 (1 + 2S_2^2 + 6\Delta^2), \qquad (2.8)$$

for the effective nonlinear susceptibility of an ensemble of spins with a general single-spin anisotropy and randomly distributed anisotropy axes [cf. Eq. (1.3)].

Equation (2.8) is the desired counterpart for the nonlinear response of the simple Eq. (2.5) for $\overline{\chi}$. The random axes average has again reduced by two the maximum order of the moments entering in the expression for the effective susceptibility. This yielded a linear susceptibility independent of the anisotropy, since the highest-order moments in the expression for χ were of second order. In contrast, although no fourth-order moments remain in $\overline{\chi}^{(3)}$, the anisotropy enters in principle in this quantity via the combinations S_2 and Δ of second-order moments. The quantities S_2 and Δ provide a measure of the deviations of the Boltzmann distribution of spin orientations from an isotropic distribution. On the one hand, the average of the second Legendre polynomial, S_2 , measures the degree of polarization of the magnetic moment along the Z axis: for $\langle z^2 \rangle \approx 1$ one has $S_2 \approx 1$, S_2 vanishes when $\langle z^2 \rangle = 1/3$, while S_2 takes negative values for $\langle z^2 \rangle < 1/3$ (spin orientations more concentrated close to the XY plane). On the other hand, Δ is a measure of the asymmetry of the equilibrium probability distribution against the transformation $x \leftrightarrow y$. Note, however, that Eq. (2.8) is independent of the signs of both S_2 and Δ .

4. Corollaries of the general result for $\bar{\chi}^{(3)}$

As the nonlinear susceptibility can be considered as a measure of the initial departure from the linear regime of the magnetization vs field curve, and this departure usually consists of a bending downwards of that curve, one is tempted to conclude that $\chi^{(3)}$ is always a negative quantity. This result is however not general and *uniaxial* spins indeed exhibit a positive equilibrium $\chi^{(3)}$ at low temperatures in a transverse probing field as a consequence of the anisotropy.¹² Nevertheless, Eq. (2.8) implies that the equilibrium nonlinear susceptibility of ensembles with randomly distributed anisotropy axes is *negative* at *all* temperatures for *any* symmetry of the single-spin anisotropy (so generalizing the result of Refs. 1 and 2 in the uniaxial case).

For isotropic spins (or at sufficiently high temperatures so that the anisotropy plays no role in determining the averages) one has $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = 1/3$. Then, $S_2 = \Delta = 0$, and the nonlinear susceptibility (2.8) reduces to the isotropic (or Langevin) result:

$$\bar{\chi}_{\rm iso}^{(3)} = -\frac{1}{45}\beta^3 m^4.$$
(2.9)

However, for magneto-anisotropic spins (or outside the hightemperature range), the quantities S_2 and Δ depart from zero yielding $|\bar{\chi}^{(3)}| \ge |\bar{\chi}^{(3)}_{iso}|$ [cf. Eqs. (2.8) and (2.9)], so that the anisotropy *always* increases the magnitude of the nonlinear response. Besides, as the thermal-equilibrium averages S_2 and Δ are temperature dependent, this increase of $|\bar{\chi}^{(3)}|$ with respect to the isotropic value is different for the different temperatures, so the overall dependence of the nonlinear susceptibility on temperature *deviates from a* β^3 *law*.

III. NONLINEAR RESPONSE IN SOME IMPORTANT CASES

After the preceding discussion on the main general consequences of the expression derived for $\bar{\chi}^{(3)}$ [Eq. (2.8)], in this section we shall particularize this formula to various cases that can be relevant in experimental systems, and study the corresponding temperature dependences of the nonlinear susceptibility.

A. Spins with uniaxial or cubic anisotropy

Whenever two of the second-order moments are equal, we can choose the coordinate axes so that those are the $\langle x^2 \rangle$ and $\langle y^2 \rangle$ moments, to get $\Delta = 0$ and reduce Eq. (2.8) to [cf. Eq. (1.3)]

$$\bar{\chi}^{(3)} = -\frac{1}{45}\beta^3 m^4 (1+2S_2^2). \tag{3.1}$$

As the condition $\langle x^2 \rangle = \langle y^2 \rangle$ is naturally obeyed by spins with *uniaxial* anisotropy, we find that Eq. (1.3) does not hold only for $\mathcal{H} \propto -z^2$, but it is valid for *any* axially symmetric anisotropy. However, this is not the whole range of validity of Eq. (3.1), as $\Delta = 0$ is also satisfied in other cases, e.g., in spin systems with *cubic* anisotropy. Here $\bar{\chi}^{(3)}$ simplifies even further, since for cubic symmetry $S_2=0$ follows from $\langle x^2 \rangle$ $= \langle y^2 \rangle = \langle z^2 \rangle = 1/3$, and hence

$$\bar{\chi}_{\rm cub}^{(3)} = -\frac{1}{45}\beta^3 m^4 \quad (\forall T).$$
 (3.2)

Notice that this result is identical with the nonlinear susceptibility in the absence of single-spin anisotropy (2.9).

In contrast, $\langle z^2 \rangle = 1/3$ is only obeyed at high temperatures by a uniaxial spin. At low temperatures, $\langle z^2 \rangle \rightarrow 1$ in the uniaxial *easy-axis* case, since \vec{m} then behaves as an effective Ising spin $(S_2 \rightarrow 1)$, while $\langle z^2 \rangle \rightarrow 0$ in the uniaxial *easyplane* case, as \vec{m} is then equivalent to an effective plane rotator $(S_2 \rightarrow -1/2)$, so that

$$\overline{\chi}_{\text{uni}}^{(3)} \simeq -\frac{1}{45} \beta^3 m^4 \quad \text{(high } T\text{)},$$

$$\overline{\chi}_{\text{uni}}^{(3)} \simeq -\frac{1}{15} \beta^3 m^4 \quad \text{(low } T\text{, easy-axis)}, \qquad (3.3)$$

$$\overline{\chi}_{\text{uni}}^{(3)} \simeq -\frac{1}{20} \beta^3 m^4 \quad \text{(low } T\text{, easy-plane)}.$$

Thus, unlike $\bar{\chi}_{cub}^{(3)}$, the nonlinear susceptibility of uniaxial spins must exhibit a *crossover* from the high-temperature isotropic regime to the low-temperature Ising-type or plane-rotator regimes, accompanied by a significant net increase of the coefficient of β^3 by a factor of 3 or 3/2, respectively. In the intermediate temperature range, $\bar{\chi}^{(3)}$ necessarily deviates from a β^3 law and the maximum deviation is reflected by a maximum in the derivative $d(T^3\bar{\chi}^{(3)})/dT$ [or equivalently in the logarithmic slope $-d \ln(-\bar{\chi}^{(3)})/dT$ [or equivalently in the logarithmic slope $-d \ln(-\bar{\chi}^{(3)})/d \ln T$; see Ref. 1]. The specific form of the crossover is governed by the form in which S_2 evolves from its high-temperature to low-temperature values, and it will be faster, the more rapidly the probability distribution concentrates close to the energy minima [for easy-axis anisotropy, this occurs when a positive quartic correction is present $\mathcal{H}^{\alpha} - (z^2 + \lambda z^4)$].

Note finally that in none of the cases considered (uniaxial or cubic) have we assumed a specific *form* for the single-spin anisotropy, but just its *symmetry*.

B. Spins with competing uniaxial and cubic anisotropies

We now consider the case in which the magnetic anisotropy of the spin includes *both* uniaxial and cubic terms. This could be an approximate description of certain magnetic nanoparticles in which the "shape" anisotropy (internal magnetostatic energy) does not completely dominate the magnetocrystalline anisotropy.

1. Hamiltonian

When the uniaxial axis is parallel to one of the cubic axes (the [001] type directions), the Hamiltonian of the spin can be written as

$$-\beta \mathcal{H} = \sigma \{ z^2 - \delta \left[(x^2 y^2 + x^2 z^2 + y^2 z^2) + \epsilon (x^2 y^2 z^2) \right] \},$$
(3.4)

where $\sigma = \beta D_u$, $\delta = D_1/D_u$, and $\epsilon = D_2/D_1$, with D_u , D_1 , and D_2 being the uniaxial, first cubic, and second cubic anisotropy constants, respectively. Concerning the relative orientation of the axes considered, we mention that because of the mechanism of formation of certain magnetic particles, there often exists a relation between the long axis of these particles (the symmetry axis of the shape anisotropy) and the crystallographic axes; the former axis has been found to be coincident with [001] or [111] type directions in ellipsoidal iron oxide particles (see Ref. 13 and references therein).

2. Temperature dependence of the nonlinear susceptibility

Figure 1(a) displays the nonlinear susceptibility of an ensemble of superparamagnets with both uniaxial and cubic anisotropy and anisotropy axes distributed at random. (The details of the calculation for this case of the quantities S_2 and Δ entering in $\overline{\chi}^{(3)}$ are given in Appendix B.) The temperature is given in units of the approximate energy barrier ΔU $\simeq D_{\rm u} + D_1/4$, i.e., as $k_{\rm B}T/\Delta U \simeq 1/[\sigma(1 + \delta/4)]$. (The exact formulas for the barrier are $\Delta U = D_{\mu}$ for $\delta < 1$ and ΔU $=D_{u}[1+(\delta/4)(1-1/\delta)^{2}]$ for $\delta > 1$, so the single expression $\Delta U \simeq D_{\rm u}(1 + \delta/4)$ conveniently interpolates between them.) From Eq. (1.2), the superparamagnetic temperature window (in which the spins display their equilibrium response) is limited from below by $\beta \Delta U = \ln(t_{\rm m}/\tau_0)$, which corresponds to the same temperature, if measured in units of ΔU , for the different cases considered. For $t_{\rm m} \sim 100$ s (ordinary "static" measurements) and $\tau_0 \sim 10^{-9}$ s (somewhere in between the values for molecular magnetic clusters and magnetic nanoparticles), the mentioned limit is located at $\ln(t_m/\tau_0) \sim 25$, which is shown in the plot by the vertical dashed line. Finally, the nonlinear susceptibility has been divided by the $\bar{\chi}^{(3)}$ of isotropic spins [Eq. (2.9)], so the graph actually shows the *anisotropy-induced* contribution to $\overline{\chi}^{(3)}$ (the β^3 laws are then represented by horizontal lines).

The nonlinear susceptibility curves exhibit the limit β^3 dependences at both high temperatures (isotropic regime) and low temperatures (Ising regime), as well as the intermediate crossover between these regimes induced by the magnetic anisotropy. It is seen that for cubic constants as large as $D_1 \sim D_u$ (for many nanoparticle systems $|D_1| \ll D_u$), the coarse features of the nonlinear susceptibility are reasonably described by those of uniaxial spins. Nevertheless, as $\delta = D_1/D_u$ increases, the onset of the anisotropy-induced contribution to $\overline{\chi}^{(3)}$ moves to lower reduced temperatures and, for sufficiently large values of δ , this contribution disappears from the observable temperature window, since the system with pure cubic anisotropy fulfills $\overline{\chi}^{(3)} = \overline{\chi}^{(3)}_{iso}$ [see Eq. (3.2)].

C. Spins with biaxial anisotropy (arbitrary shape anisotropy)

1. Hamiltonian

The final case that we consider is that of spins with biaxial anisotropy

$$-\beta \mathcal{H} = \sigma_x x^2 + \sigma_y y^2 + \sigma_z z^2, \quad 0 \le \sigma_x \le \sigma_y \le \sigma_z,$$



FIG. 1. Nonlinear susceptibility of an ensemble of superparamagnets with randomly distributed anisotropy axes and (a) uniaxial plus cubic anisotropy [for different values of $\delta/4$ shown in the plot and $\epsilon = 0$; see Hamiltonian (3.4)] and (b) biaxial anisotropy [for different values of ε shown in the plot; see Hamiltonian (3.5)]. The temperature is represented in the dimensionless forms: (a) $T^* = 1/[\sigma(1 + \delta/4)]$ and (b) $T^* = 1/\sigma$. The temperature window that can be observed experimentally with a measurement time $t_m \sim 100$ s for $\tau_0 \sim 10^{-9}$ s is limited by the vertical dashed lines [shown only for $\varepsilon = 0$, 1/2, and 3/4 in (b)]. The nonlinear susceptibility has been divided by $\bar{\chi}_{iso}^{(3)}$ [the nonlinear susceptibility of isotropic spins (2.9)], in order to isolate the anisotropy-induced contribution to $\bar{\chi}^{(3)}$.

whose significance stems from the following considerations. On the one hand, Brown and Morrish¹⁴ showed that, as far as the energy is concerned, a uniformly magnetized particle with *arbitrary* shape is equivalent to a particle (of the same volume) with the shape of a suitably chosen general ellipsoid (see also Ref. 15, p. 128). On the other hand, the shape anisotropy of one such general ellipsoid is given by the above expression with $\sigma_i = \beta(v M_s^2/2) N_i$, where v is the volume of the particle, M_s its spontaneous magnetization, and the N_i are the (ellipsoid) demagnetization factors. Accordingly, the biaxial Hamiltonian is the most general expression for single-domain nanoparticles in which the shape anisotropy largely dominates the other contributions to the anisotropy (magnetocrystalline, surface, etc.).

On using $x^2 = 1 - y^2 - z^2$, introducing the parameters $\sigma \equiv \sigma_z - \sigma_x$ and $\varepsilon \equiv (\sigma_y - \sigma_x)/(\sigma_z - \sigma_x)$, which satisfy $\sigma \ge 0$

and $0 \le \varepsilon \le 1$, and omitting constant additive terms, we can cast the Hamiltonian into the form (now explicitly biaxial)

$$-\beta \mathcal{H} = \sigma(z^2 + \varepsilon y^2). \tag{3.5}$$

In the case of general shape anisotropy we would have $\sigma = \beta(vM_s^2/2)(N_z - N_x)$, while $\varepsilon = (N_y - N_x)/(N_z - N_x)$ is a geometrical factor only. Notice that there are two equivalent energy minima at $(x, y, z) = (0, 0, \pm 1)$, whereas $(0, \pm 1, 0)$ are saddle points, so the relevant energy barrier is given by $\beta \Delta U = \sigma(1 - \varepsilon)$. Note also that for $\varepsilon \rightarrow 0$ we recover the simplest uniaxial anisotropy, while $\varepsilon \rightarrow 1$ also leads to uniaxial anisotropy, $-\beta \mathcal{H}|_{\varepsilon=1} = \sigma(1 - x^2)$, but with a *plane* of easy magnetization (the *YZ* plane). Therefore, as $|\overline{\chi}^{(3)}|$ is smaller for easy-plane anisotropy [cf., for instance, the low-*T* results of Eq. (3.3)] we can expect that the magnitude of the nonlinear response will decrease with increasing ε . We shall confirm this below and see the specific form in which this takes place.

2. Temperature dependence of the nonlinear susceptibility

Figure 1(b) shows the nonlinear susceptibility of an ensemble of superparamagnets with biaxial anisotropy and randomly distributed anisotropy axes. (The details of the calculation of the quantities entering in the expression for $\overline{\chi}^{(3)}$ are given in Appendix B.) The temperature has been represented by $1/\sigma$, and the temperature window that can be observed with a measurement time $t_m \sim 100$ s, for $\tau_0 \sim 10^{-9}$ s, is limited from below by $\beta \Delta U = \sigma (1-\varepsilon) \sim 25$ in each case (shown by the vertical dashed lines for $\varepsilon = 0$, 1/2, and 3/4). Again, the nonlinear susceptibility has been divided by that of isotropic spins [Eq. (2.9)], in order to isolate the anisotropy-induced contribution to $\overline{\chi}^{(3)}$.

The graph shows that, for values of the biaxial parameter as large as $\varepsilon \sim 1/2$, the overall features of the nonlinear susceptibility curves are not too different from those of the easyaxis uniaxial case. We also see that, as anticipated above, the anisotropy-induced contribution to $\overline{\chi}^{(3)}$ decreases monotonically with increasing ε and, as $\varepsilon \rightarrow 1$, it tends to the values corresponding to easy-plane anisotropy. However, this does not take place uniformly in T and, for $\varepsilon \ge 0.9$, a second crossover to the Ising regime at lower temperatures can be observed [if we analyzed $d(T^3\bar{\chi}^{(3)})/dT$, we would find a second maximum in this derivative]. This crossover is best understood by rewriting the biaxial Hamiltonian as $-\beta \mathcal{H}/\sigma = \varepsilon (1-x^2) + (1-\varepsilon)z^2$, which corresponds to easyplane anisotropy with an easy axis in the plane. Then, for large values of ε , the preferred direction introduced in the easy plane by $(1-\varepsilon)z^2$ becomes relevant at sufficiently low temperatures $[1/\sigma \sim (1-\varepsilon) \ll 1]$, causing the final crossover to the Ising regime.

IV. SUMMARY AND CONCLUSIONS

We have studied the equilibrium nonlinear response of noninteracting superparamagnets with a general single-spin anisotropy. We have obtained a general expression for the nonlinear susceptibility in the experimentally important case of anisotropy axes distributed at random [Eq. (2.8)], which can be considered as the generalization for the nonlinear response of the simple formula for the averaged linear susceptibility $\overline{\chi} = \beta m^2/3$. The expression derived has allowed us to demonstrate some simple but rather general results for spin ensembles with random anisotropy: (i) $\overline{\chi}^{(3)}$ is always negative, (ii) unlike $\overline{\chi}$, the nonlinear susceptibility remains anisotropy dependent after the random axes average (except for systems satisfying $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle$, for which $\overline{\chi}^{(3)}$ is equal to that of isotropic spins), (iii) the single-spin anisotropy always increases the magnitude of the nonlinear response, and (iv) since this increase depends on temperature, $\overline{\chi}^{(3)}$ departs from the common $\overline{\chi}^{(3)} \propto \beta^3$ laws.

The general formula derived has been particularized to various situations that might be relevant in experimental systems. For spins with competing uniaxial and cubic anisotropies we have found that $\bar{\chi}^{(3)}$ exhibits an anisotropy-induced crossover from the isotropic to the Ising-type behavior, but this crossover is displaced out of the equilibrium temperature window as the cubic contribution dominates. For spins with biaxial anisotropy, the crossover never disappears from the superparamagnetic window, though its effects on the nonlinear response are reduced as the parameter measuring the biaxial character increases. Nevertheless, for large values of this parameter, following the crossover at lower temperatures to the Ising regime.

We finally remark that the monitoring of the different anisotropy regimes provided by the nonlinear susceptibility (which has no counterpart in the averaged linear susceptibility), could in principle be reversed to extract information about the magnetic anisotropy of superparamagnets from simple nonlinear susceptibility measurements.

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APPENDIX A: GENERAL DEFINITIONS AND EXPRESSIONS FOR THE SUSCEPTIBILITIES

In this appendix various definitions (tensorial and effective) of the linear and nonlinear susceptibilities are given, as well as the expressions for these quantities in terms of thermal-equilibrium averages of the unperturbed spins.

1. Tensor definitions

Let us consider a classical spin \vec{m} with (unperturbed) Hamiltonian $\mathcal{H}(\vec{m})$ and subjected to a probing field \vec{b} . The response of the spin to the perturbation can be characterized by the thermal-equilibrium average $\langle \vec{m} \rangle$, taken with respect to the Boltzmann distribution of spin orientations associated with the total Hamiltonian $\mathcal{H}_{T} = \mathcal{H} - \vec{m} \cdot \vec{b}$. When the perturbation is sufficiently weak, a suitable quantity describing the spin response is the *linear* susceptibility, which is defined as the second-rank tensor

$$\chi_{ij} = \frac{\partial \langle m_i \rangle}{\partial b_j} \bigg|_{b=0}.$$
 (A1)

The response to stronger perturbations can be characterized by higher-order derivatives and, for moderate fields, it is sufficient to introduce the *quadratic* and *cubic* susceptibility tensors, namely,

$$\chi_{ijk}^{(2)} = \frac{1}{2} \left. \frac{\partial^2 \langle m_i \rangle}{\partial b_j \partial b_k} \right|_{b=0}, \quad \chi_{ijkl}^{(3)} = \frac{1}{6} \left. \frac{\partial^3 \langle m_i \rangle}{\partial b_j \partial b_k \partial b_l} \right|_{b=0}.$$
(A2)

Using these definitions, the Taylor expansion of $\langle m_i \rangle$ with respect to the probing field can simply be written as

$$\langle \Delta m_i \rangle \simeq \sum_j \chi_{ij} b_j + \sum_{jk} \chi^{(2)}_{ijk} b_j b_k + \sum_{jkl} \chi^{(3)}_{ijkl} b_j b_k b_l,$$

where Δm_i stands for $m_i - \langle m_i \rangle |_{b=0}$.

2. Effective susceptibilities

Let us now consider the projection of the thermalequilibrium average of \vec{m} on the probing-field direction. Since $\langle \Delta \vec{m} \cdot \vec{b} \rangle = \sum_i \langle \Delta m_i \rangle b_i$, we get from the preceding Taylor expansion:

$$\langle \Delta \vec{m} \cdot \hat{b} \rangle \simeq \left(\sum_{ij} \chi_{ij} \alpha_i \alpha_j \right) b + \left(\sum_{ijk} \chi^{(2)}_{ijk} \alpha_i \alpha_j \alpha_k \right) b^2$$
$$+ \left(\sum_{ijkl} \chi^{(3)}_{ijkl} \alpha_i \alpha_j \alpha_k \alpha_l \right) b^3,$$
(A3)

where we have introduced the unit vector $\hat{b} = \tilde{b}/b$ and the associated direction cosines $\alpha_i = b_i/b$. The quantities in the brackets define the scalar *effective* susceptibilities

$$\chi = \sum_{ij} \chi_{ij} \alpha_i \alpha_j \tag{A4}$$

$$\chi^{(2)} = \sum_{ijk} \chi^{(2)}_{ijk} \alpha_i \alpha_j \alpha_k \tag{A5}$$

$$\chi^{(3)} = \sum_{ijkl} \chi^{(3)}_{ijkl} \alpha_i \alpha_j \alpha_k \alpha_l, \qquad (A6)$$

which are the quantities commonly obtained in experiments.

3. Susceptibilities in terms of averages in the absence of the probing field

Let us finally express the susceptibilities in terms of averages of \vec{m} taken in the zero-probing-field limit. The corresponding calculations can be carried out by starting from the total Hamiltonian $\mathcal{H}_{\rm T} = \mathcal{H} - \vec{m} \cdot \vec{b}$, where the actual form of the unperturbed Hamiltonian \mathcal{H} is not required, and setting $\vec{b} = \vec{0}$ at the end. (Together with magnetic anisotropy terms, \mathcal{H} could include the coupling with an external bias field \vec{B} .)

The thermal-equilibrium average of any quantity $A(\vec{m})$ can be written as

$$\langle A \rangle = \frac{1}{\mathcal{Z}} \int d\Omega \ A(\cos \vartheta, \varphi) e^{-\beta \mathcal{H}_{\mathrm{T}}}.$$
 (A7)

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where we have introduced the notation $\int d\Omega \equiv \int_{-1}^{1} d(\cos \vartheta) \int_{0}^{2\pi} (d\varphi/2\pi)$, the spherical coordinates are defined by $m_z = m \cos \vartheta$ and $m_x + i m_y = m \sin \vartheta \exp(i\varphi)$, and $\mathcal{Z} = \int d\Omega \exp(-\beta \mathcal{H}_T)$ is the partition function. The general derivative $\partial \langle A \rangle / \partial b_j$ can easily be taken by using $-\partial \mathcal{H}_T / \partial b_j = m_j$, and reads

$$\frac{\partial \langle A \rangle}{\partial b_{j}} = \beta [\langle A m_{j} \rangle - \langle A \rangle \langle m_{j} \rangle]. \tag{A8}$$

The application of this result to $A = m_i$ gives

$$\frac{\partial \langle m_i \rangle}{\partial b_j} = \beta [\langle m_i m_j \rangle - \langle m_i \rangle \langle m_j \rangle], \tag{A9}$$

which when evaluated at b=0 and introduced in Eq. (A1), yields the familiar expression for χ_{ij} in terms of averages taken with respect to the Boltzmann distribution associated to the unperturbed Hamiltonian \mathcal{H} .

The nonlinear susceptibilities can be expressed analogously. For instance, if we use Eq. (A8) also for $A = m_i m_j$, we can readily differentiate Eq. (A9), to obtain

$$\frac{\partial^2 \langle m_i \rangle}{\partial b_j \partial b_k} = \beta^2 [\langle m_i m_j m_k \rangle - \langle m_i m_j \rangle \langle m_k \rangle - \langle m_i m_k \rangle \langle m_j \rangle - \langle m_i m_k \rangle \langle m_i \rangle + 2 \langle m_i \rangle \langle m_j \rangle \langle m_k \rangle],$$

from which we can get the quadratic susceptibility $\chi_{ijk}^{(2)}$. Finally, we can similarly differentiate this result to obtain the third-order derivatives, getting

$$\begin{aligned} \frac{\partial^{3} \langle m_{i} \rangle}{\partial b_{j} \partial b_{k} \partial b_{l}} &= \beta^{3} \{ \langle m_{i} m_{j} m_{k} m_{l} \rangle - \langle m_{i} m_{j} m_{k} \rangle \langle m_{l} \rangle \\ &- \langle m_{i} m_{j} m_{l} \rangle \langle m_{k} \rangle - \langle m_{i} m_{k} m_{l} \rangle \langle m_{j} \rangle \\ &- \langle m_{j} m_{k} m_{l} \rangle \langle m_{i} \rangle - \langle m_{i} m_{j} \rangle \langle m_{k} m_{l} \rangle \\ &- \langle m_{i} m_{k} \rangle \langle m_{j} m_{l} \rangle - \langle m_{j} m_{k} \rangle \langle m_{i} m_{l} \rangle \\ &+ 2[\langle m_{i} m_{j} \rangle \langle m_{k} \rangle \langle m_{l} \rangle + \langle m_{k} m_{l} \rangle \langle m_{i} \rangle \langle m_{j} \rangle \\ &+ \langle m_{i} m_{k} \rangle \langle m_{j} \rangle \langle m_{l} \rangle + \langle m_{j} m_{l} \rangle \langle m_{i} \rangle \langle m_{k} \rangle \\ &+ \langle m_{j} m_{k} \rangle \langle m_{i} \rangle \langle m_{l} \rangle + \langle m_{i} m_{l} \rangle \langle m_{j} \rangle \langle m_{k} \rangle] \\ &- 6 \langle m_{i} \rangle \langle m_{l} \rangle \langle m_{k} \rangle .\end{aligned}$$

On evaluating this formula at b=0 and multiplying by 1/6 one gets $\chi_{ijkl}^{(3)}$. These results illustrate the general rule: the *n*th-order derivatives of the first-order moments (i.e., the susceptibilities) can be expressed in terms of moments of the unperturbed probability distribution of order not higher than n+1.

APPENDIX B: CALCULATION OF S_2 AND Δ

In this appendix we derive (single-integral) formulas for the quantities $S_2 = (3\langle z^2 \rangle - 1)/2$ and $\Delta = (\langle y^2 \rangle - \langle x^2 \rangle)/2$, which enter in the general expression (2.8) for the effective nonlinear susceptibility, in the cases of spins with competing uniaxial and cubic anisotropies [Hamiltonian (3.4)] and biaxial anisotropy [Hamiltonian (3.5)].

1. Competing uniaxial and cubic anisotropies

Note first that in the coordinate system in which the Hamiltonian (3.4) has been written, the cross correlations $\langle m_i m_j \rangle$ vanish for $i \neq j$, so one can use Eq. (2.8) to calculate the nonlinear susceptibility. On expressing the Hamiltonian in terms of the (canonical) variables z and φ , we have

$$-\beta \mathcal{H} = \sigma z^{2} - \sigma \delta \left[z^{2} (1 - z^{2}) + \frac{1}{8} (1 - z^{2})^{2} (1 + \epsilon z^{2}) \right] + \frac{1}{8} \sigma \delta (1 - z^{2})^{2} (1 + \epsilon z^{2}) \cos 4\varphi,$$
(B1)

where only the last term breaks the axial symmetry. In order to calculate averages of functions of z alone (or the partition function), we can deal with this term by using the identity

$$\frac{1}{2\pi} \int_0^{2\pi} d\varphi \, e^{\xi \cos(n\varphi)} \stackrel{n\varphi=\varphi'}{=} \frac{1}{2\pi} \int_0^{2\pi} d\varphi' e^{\xi\cos\varphi'} = I_0(\xi),$$
(B2)

where $I_0(\xi)$ is the modified Bessel function of the first kind of order 0, and to get the first equality we have used the periodicity of the integrand and that *n* is an integer.

The application of Eq. (B2) [with n=4 and $\xi = \sigma \delta(1 - z^2)^2 (1 + \epsilon z^2)/8$] to integrals of the type mentioned,

$$F \equiv \int_{-1}^{1} dz \int_{0}^{2\pi} \frac{d\varphi}{2\pi} f(z) e^{-\beta \mathcal{H}(z,\varphi)},$$
 (B3)

gives

$$F = \int_{-1}^{1} dz f(z) I_0[\frac{1}{8}\sigma\delta(1-z^2)^2(1+\epsilon z^2)]$$

$$\times \exp\{\sigma z^2 - \sigma\delta[z^2(1-z^2) + \frac{1}{8}(1-z^2)^2(1+\epsilon z^2)]\}.$$

Then, on introducing an effective (temperature-dependent) uniaxial Hamiltonian

$$-\beta \mathcal{H}_{\rm eff}(z) = \sigma z^2 - \sigma \delta \left[z^2 (1 - z^2) + \frac{1}{8} (1 - z^2)^2 (1 + \epsilon z^2) \right] + \ln I_0 \left[\frac{1}{8} \sigma \delta (1 - z^2)^2 (1 + \epsilon z^2) \right], \tag{B4}$$

we can compactly write

$$F = \int_{-1}^{1} dz f(z) \exp[-\beta \mathcal{H}_{\text{eff}}(z)].$$
 (B5)

For instance, the average of the second Legendre polynomial [case $f(z) = \mathcal{Z}^{-1}(3z^2 - 1)/2$] reads

$$S_{2} = \frac{1}{\mathcal{Z}} \int_{-1}^{1} dz \frac{1}{2} (3z^{2} - 1) \exp[-\beta \mathcal{H}_{\text{eff}}(z)],$$

where the partition function [f(z)=1] is given by the natural expression $\mathcal{Z}=\int_{-1}^{1} dz \exp[-\beta \mathcal{H}_{eff}(z)]$. Finally, as the starting Hamiltonian (3.4) is invariant against the transformation $x \leftrightarrow y$, we find $\Delta = 0$ in this case, so the simplified form (3.1) for $\overline{\chi}^{(3)}$ holds again (the same would occur if the uniaxial axis pointed along a [111] type direction).

2. Biaxial anisotropy

Let us first rewrite the Hamiltonian (3.5) for the biaxial spin in terms of the variables z and φ ,

$$-\beta \mathcal{H} = \frac{1}{2}\sigma\varepsilon + \sigma(1 - \frac{1}{2}\varepsilon)z^2 - \frac{1}{2}\sigma\varepsilon(1 - z^2)\cos 2\varphi.$$

This form is very convenient because to calculate integrals of the type (B3), we can deal with the nonaxially symmetric term in a manner analogous to that used in the uniaxial plus cubic case. Thus, by means of Eq. (B2) [now with n=2 and $\xi = -\sigma \varepsilon (1-z^2)/2$] we find

$$F = \int_{-1}^{1} dz f(z) \exp\left[\frac{1}{2}\sigma\varepsilon + \sigma(1 - \frac{1}{2}\varepsilon)z^2\right] I_0\left[\frac{1}{2}\sigma\varepsilon(1 - z^2)\right],$$

where $I_0(-\xi) = I_0(\xi)$ has been taken into account. Therefore, if we introduce the following effective uniaxial Hamiltonian [cf. Eq. (B4)]

$$-\beta \mathcal{H}_{\text{eff}}(z) = \frac{1}{2}\sigma\varepsilon + \sigma(1 - \frac{1}{2}\varepsilon)z^2 + \ln I_0[\frac{1}{2}\sigma\varepsilon(1 - z^2)],$$

we can again write F as in Eq. (B5).

The average of the second Legendre polynomial can be obtained by inserting $f(z) = Z^{-1}(3z^2 - 1)/2$ in Eq. (B5). Besides, since the partition function is defined as

$$\mathcal{Z} = \int_{-1}^{1} dz \int_{0}^{2\pi} \frac{d\varphi}{2\pi} \exp[\sigma(z^2 + \varepsilon y^2)],$$

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one can obtain $\langle y^2 \rangle$ (and hence Δ) from the derivative $\langle y^2 \rangle = (\sigma Z)^{-1} (\partial Z/\partial \varepsilon)$. On this doing with the partition function written as $Z = \int_{-1}^{1} dz \exp[-\beta \mathcal{H}_{eff}(z)]$, we get

$$\langle y^{2} \rangle = \frac{1}{\mathcal{Z}} \int_{-1}^{1} dz \, \frac{1}{2} (1 - z^{2}) \left(\frac{I_{1}}{I_{0}} \right) \bigg|_{\sigma \varepsilon (1 - z^{2})/2} \exp[-\beta \mathcal{H}_{\text{eff}}(z)]$$

$$+ \frac{1}{\mathcal{Z}} \int_{-1}^{1} dz \, \frac{1}{2} (1 - z^{2}) \exp[-\beta \mathcal{H}_{\text{eff}}(z)],$$

$$\underbrace{(1 - (z^{2}))/2}_{(1 - (z^{2}))/2}$$

where $I_1(\xi) = dI_0/d\xi$ is the modified Bessel function of the first kind of order 1. By comparing with $\langle y^2 \rangle = (1 - \langle z^2 \rangle)/2 + \Delta$, one realizes that the first integral in the preceding equation is actually Δ , so we finally obtain for the quantities entering in the expression for $\overline{\chi}^{(3)}$:

$$S_{2} = \frac{1}{\mathcal{Z}} \int_{-1}^{1} dz \frac{1}{2} (3z^{2} - 1) \exp[-\beta \mathcal{H}_{\text{eff}}(z)],$$

$$\Delta = \frac{1}{\mathcal{Z}} \int_{-1}^{1} dz \frac{1}{2} (1 - z^{2}) \left(\frac{I_{1}}{I_{0}}\right) \Big|_{\sigma \varepsilon (1 - z^{2})/2} \exp[-\beta \mathcal{H}_{\text{eff}}(z)].$$

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