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Equilibrium susceptibilities of superparamagnets: longitudinal and transverse, quantum and classical

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Abstract

The equilibrium susceptibility of uniaxial paramagnets is studied in a unified framework which permits us to connect traditional results of the theory of quantum paramagnets, $S = 1/2, 1, 3/2, \dots$, with molecular magnetic clusters, $S \sim 5, 10, 20$ all the way up ($S = 30, 50, 100, \dots$) to the theory of classical superparamagnets. This is done using standard tools of quantum statistical mechanics and linear-response theory (the Kubo correlator formalism). Several features of the temperature dependence of the susceptibility curves (crossovers, peaks, deviations from Curie law) are studied and their scalings with S identified and characterized. Both the longitudinal and transverse susceptibilities are discussed, as well as the response of the ensemble with anisotropy axes oriented at random. For the latter case a simple approximate formula is derived too, and its range of validity assessed, which could be used in the modelization of experiments.

1. Introduction

Modern magnetism, quantum mechanics and statistical mechanics have a long history of common development since the beginning of the 20th century. Behind it are the names of the pioneers: Langevin, Brillouin, Bohr and Van Leeuwen, Landau, Van Vleck, Pauli, etc. After spectroscopy, magnetism helped the most in our understanding of the atom. Besides, some of the earliest successes of the Gibbs–Boltzmann distribution were indeed applications to magnetic problems [1]. Initially, applications to the simplest magnetic systems, atoms or small molecules with a permanent magnetic moment: *paramagnets*.

When the magnetic moments are brought together they can interact (by dipole–dipole coupling or by ‘exchange’, due to the Pauli principle). Then a new game starts, with the possibility of long-range order, spin waves, etc. Another important player, when the spins are placed in a molecular complex or in a solid, is the magnetic anisotropy. The spin–orbit coupling allows a magnetic moment to sense the electric field from neighboring ions. This gives rise to preferred orientations, according to the space symmetry of

the compound/solid: cubic, tetragonal (biaxial), hexagonal (\sim uniaxial), etc [2, 3].

The magnetic anisotropy can also interplay with the spin–spin interactions, modifying the spin-wave dispersion relations or determining the spin orientation inside ordered ‘domains’ [2, 3]. If there is no room for domain walls, as in sufficiently fine particles, the anisotropy would dictate the stable orientations of the whole magnetic moment (the dipole–dipole interaction also plays a role, as it ‘adds’ to the anisotropy). Those stable orientations are the basis of using such particles as physical bits.

1.1. Quantum and classical superparamagnets

One more element sets in if the temperature is high enough (but still below the ordering temperatures), or when the particle is sufficiently small (\sim nm). Then, by thermal activation, the net moment can overcome the anisotropy energy barriers and flip back and forth between the minima [4, 5]. This is a nightmare for magnetic recording [6], but a blessing for new phenomenology. Inside we have an ordered magnet, which when seen from the outside resembles a paramagnet,

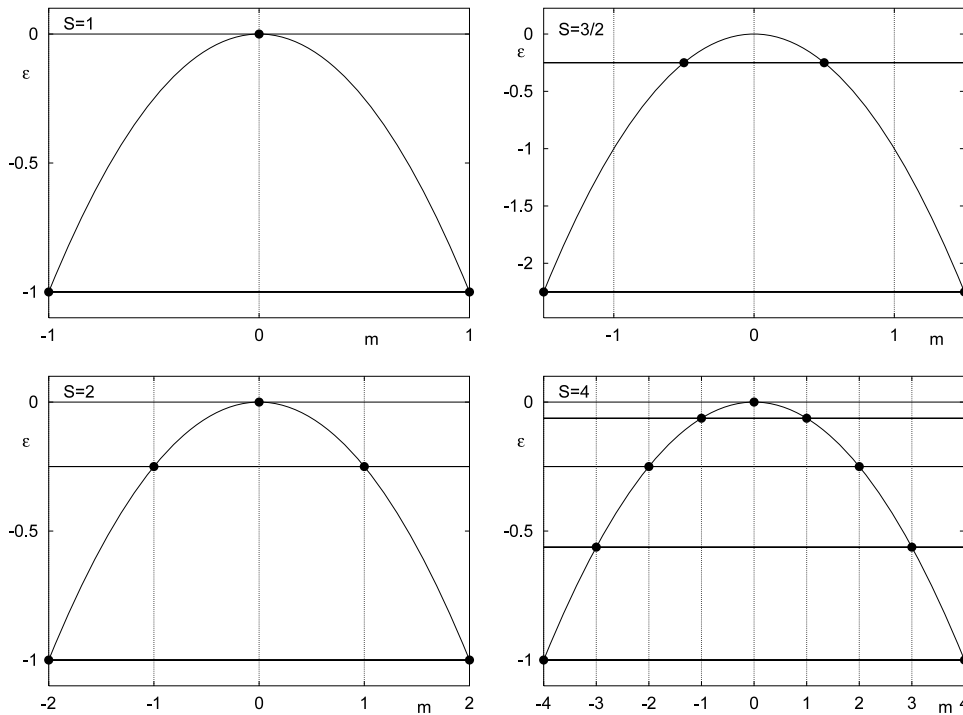


Figure 1. Energy levels $\varepsilon_m = -Dm^2 - B_z m$ of anisotropic spins $S = 1, 3/2, 2$ and 4 at zero field. For $S = 1$ and $3/2$ we set $D = 1$. For $S = 2$ and 4 , the anisotropy constant is scaled as $D = 1/S^2$, so that these spins have the same energy barrier as $S = 1$.

but with a very large magnetic moment, $S \sim 100\text{--}1000$ —*superparamagnetism*. Yet another connection with statistical mechanics is established as the non-equilibrium orientational distribution of those ‘classical’ spins is described with the tools of Brownian/stochastic dynamics, e.g. Fokker–Planck or Langevin equations [7–9].

The 1980s and 1990s brought, through the advances in chemical synthesis, a new member of the paramagnetic family, *molecular magnetic clusters* [10] (also referred to as *single-molecule magnets*). These are made of complex molecules with a net spin $S \sim 5, 10, 20$, somewhere in between the traditional paramagnets and the superparamagnets. But, contrary to magnetic nanoparticles, they are assembled in molecular crystals, minimizing extrinsic sources of dispersion (in size, anisotropy parameters, etc) and making the comparison between experiment and theory cleaner.

As for the static part of the magnetic anisotropy, it can be quite large in molecular magnets, so the stable orientations could provide the basis of a quantum bit. Nevertheless, environmental effects (decoherence in particular) emerge already from their own nuclear spins or from the dynamical part of the spin–orbit coupling (neighboring ions are never static; the lattice oscillations modulate the local electric field, which modifies the orbital motions, eventually affecting \vec{S}). Again, a curse for technology, but a blessing for physics [11]. The total system can be described by a spin–phonon Hamiltonian [12–14] and constitutes a neat realization of the spin-boson paradigm of the theory of quantum dissipative systems [15], but with a $S \geq 1/2$ immersed in a bath of true ‘harmonic oscillators’ (the lattice phonons).

1.2. The spin Hamiltonian

The theoretical description of paramagnets starts with a spin Hamiltonian, where one replaces the true microscopic Hamiltonian (or a part of it) by one written in terms of spin energy levels and operators (a procedure initiated by Heisenberg, Dirac and Van Vleck [16, section 72]). This provides an equivalent description of the statics (based on the spectrum) and of part of the dynamics. The inner complexities (symmetrization of wavefunctions, local fields, spin–orbit coupling) are left in the background and we only see their effect through the spin Hamiltonian [1, 12, 16].

For many classical superparamagnets [17] and molecular clusters [10], a good first approximation is provided by

$$\mathcal{H}_0 = -DS_z^2 - \vec{B} \cdot \vec{S}, \quad (1.1)$$

with D the uniaxial anisotropy constant. $D > 0$ produces two preferred spin orientations (the ‘bit’, figure 1) and brings in the physics of bistable systems (e.g. thermal activation over a potential barrier). But there is also a rich ‘coherent’ or transverse dynamics [12, 18], with spin resonances, absorption peaks, etc⁴.

⁴ The big-spin Hamiltonian (1.1) is also an effective description of a collection of N two-level systems (not necessarily magnetic), used in atomic optics since the 1970s [19]. Non-interacting entities correspond to $D = 0$, while $D \neq 0$ with a transverse field B_x describes certain types of uniform interaction (the Lipkin–Meshkov–Glick model originally from nuclear physics). The theoretical work on this front was revived with the boom in cold gases and condensates [20, 21].

1.3. The magnetic susceptibility and linear-response theory

Most of what we know about magnets, and even their names and the ways we classify them, is based on their characteristic response [1]. That is, on how they respond to the application of controlled magnetic field probes. When the probes are small enough, linearizations and perturbation theory, in its different guises, can be used by the theorist.

In molecular magnetism a procedure due to Van Vleck [1, chapter 3] became quite popular. The energy levels of a paramagnet, in the presence of the probing field, are obtained using quantum-mechanical perturbation theory and the result plugged into a Gibbs–Boltzmann formula. In other, more complicated problems of theoretical magnetism (e.g. quantum spin chains [22–25] or inner structure of molecular clusters [26]) other tools from linear-response theory are employed. The Kubo correlator, in particular, provides a formal general solution for the response functions, the susceptibility χ , without invoking perturbed levels at all (the usual ‘magic’ of linear-response theory [27, 28]).

1.4. Our approach and goals

We aim to calculate the equilibrium linear response for paramagnets with simple anisotropies, but in a way that could connect the traditional results for quantum paramagnets, all the way up to the results of classical superparamagnetic theory.

The approach of Van Vleck, at least in its popular form of diagonalize and linearize [29, 30], becomes awkward for moderately small S . Therefore we will resort to the Kubo correlator formalism and particularize it with the (super)paramagnetic problem in mind.

Schematically, the approach takes two steps (section 2): (1) obtain the correlator $\int_0^\beta d\sigma \text{Tr}[e^{(\beta-\sigma)\mathcal{H}_0} V e^{+\sigma\mathcal{H}_0} V]$, and sandwich here and there identities $\mathbb{I} = \sum_m |m\rangle\langle m|$ formed with the unperturbed levels $\mathcal{H}_0|m\rangle = \varepsilon_m|m\rangle$. This gives a susceptibility $\chi \sim \beta \sum_{mn} e^{-\beta\varepsilon_m} |V_{mn}|^2 K[\beta(\varepsilon_m - \varepsilon_n)]$ with the Kubo function $K(X) = (e^X - 1)/X$ evaluated at the level differences. (2) Next, for uniaxial problems, $\mathcal{H}_0 = -DS_z^2 - B_z S_z$, the matrix elements of the perturbation V simplify, $V_{mn} \sim V_{\parallel}\delta_{m,n} + V_{\perp}\delta_{m,n\pm 1}$, and the above χ can be reduced to a single sum over the unperturbed spectrum (in the line of naive linear-response theory). One component of χ , the longitudinal susceptibility, comes from the part of V commuting with \mathcal{H}_0 ; the non-commuting part gives the transverse susceptibility (equations (2.25)–(2.26)).

Some advantages of this approach are: (1) the intermediate step of getting eigenvalues in the presence of the perturbation is bypassed, (2) there is no small-denominator problem; $K(0) = 1$ ensures automatically the finiteness of the perturbative result, without the need of manual pairing of degenerate levels or the like [31] and (3) the susceptibility formula, expressed as a *single* sum over the spin levels m , is ready to use for any S .

As a check, we recover in section 3 a number of traditional results for paramagnets, including the transverse response of small spins $S = 1$ and $3/2$. Then, we will move on to arbitrary S in section 4 and discuss some features of the temperature-dependent susceptibility curves, like crossovers, peaks and the isotropy of χ in the randomly oriented ensemble. We will study

how these features evolve with S under appropriate scalings (figure 1).

The interest in the $\chi(T)$ curves stems from their routine use as indicators of anisotropies, interactions between spins, etc [29, 30, 32]. Therefore it is important to understand well the paramagnetic ‘ideal gas’ (as the implicit reference curve in those procedures), including the effect of simple anisotropies (e.g. uniaxial, biaxial, etc). We hope that our results will convince the reader of the advantage of having a unified framework for the response of the whole paramagnetic family, from the traditional members, then molecular magnetic clusters, up to classical superparamagnets.

2. Derivation of the susceptibility

Instead of starting writing down directly the linear susceptibility in terms of a Kubo correlator, we will briefly discuss its basis on plain statistical–mechanical perturbation theory. This will make the presentation more self-contained and will hint at how to proceed if higher orders are required, beyond linear response.

2.1. Statistical mechanical preliminaries

Statistical mechanics is about computing averages, variances/dispersions, etc, for a given system with the sole input of the *system Hamiltonian* \mathcal{H} and a few parameters incorporating the effect/presence of a thermalizing environment (like $\beta = 1/T$, chemical potentials, etc). The averages are generated from the *density matrix* $\varrho \propto e^{-\beta\mathcal{H}}$, and for a given operator quantity Q one forms the following basis-independent object:

$$\langle Q \rangle = \text{Tr}(\varrho Q) = \sum_{mn} \varrho_{mn} Q_{nm}. \quad (2.1)$$

For consistency of the definition, ϱ is ‘normalized’ to have unit trace $\text{Tr}(\varrho) = 1$ (so the average of a constant is the constant itself):

$$\varrho = e^{-\beta\mathcal{H}}/\mathcal{Z}, \quad \mathcal{Z} = \text{Tr} e^{-\beta\mathcal{H}}. \quad (2.2)$$

The normalization function, \mathcal{Z} , plays a central role in several parts of the formalism. In particular, as an auxiliary/abridged generator of averages (by differentiation) with the advantage of being a scalar instead of an operator.

2.1.1. Response observables. Let us imagine that the quantity we are interested in can be obtained from the Hamiltonian by differentiation:

$$Q = -\partial_f \mathcal{H} \quad (\text{operator identity}). \quad (2.3)$$

Say, the total Hamiltonian is of the form $\mathcal{H} = \mathcal{H}_0 - fQ$, as in the examples of force–coordinate, $-Fx$, or field–dipole/spin, $-\vec{B} \cdot \vec{S}$. Then the average of Q can be obtained from the partition function as follows:

$$\langle Q \rangle = \frac{1}{\mathcal{Z}} \frac{1}{\beta} \text{Tr}(\partial_f e^{-\beta\mathcal{H}}) = \frac{1}{\mathcal{Z}} \partial_{(\beta f)} \text{Tr}(e^{-\beta\mathcal{H}}) = \frac{\mathcal{Z}'}{\mathcal{Z}}. \quad (2.4)$$

Here (\prime) denotes derivative with respect to the ‘thermal’ force/field parameter $\xi := \beta f$ entering in $-\beta\mathcal{H} = -\beta\mathcal{H}_0 + \xi Q$.⁵

We will refer to the average of a quantity Q derivable from the Hamiltonian as above as a *response observable*. This definition does not include pure thermal quantities, like the thermodynamical energy or the specific heat, although these can be obtained by differentiating \mathcal{Z} with respect to $\beta = 1/T$.

2.1.2. Susceptibility and derivatives of \mathcal{Z} . As the force/field parameter f is at our disposal, we can change f and from the induced change in $\langle Q \rangle$ learn how the system ‘responds’. A natural quantity then arises:

$$\chi = \partial_f \langle Q \rangle, \quad (2.5)$$

quantifying the sensitivity of the system to changes in f , and for this reason called the *susceptibility*. χ is thus a second derivative of \mathcal{Z} , and if we keep on using $\xi = \beta f$ and $(\prime) = \partial_\xi$, we have $\chi = \beta[(\mathcal{Z}''/\mathcal{Z}) - (\mathcal{Z}'/\mathcal{Z})^2]$, where the square bracket is merely $(\mathcal{Z}'/\mathcal{Z})'$.

We can think that f is the part of the force/field that we change (the probe) over a fixed bias f_0 . Then, from $-(f_0 + f)Q$ we can move $-f_0Q$ into the unperturbed part \mathcal{H}_0 , and eventually evaluate our derivatives at $f = 0$ (linear susceptibility). Then, all we need to do is to obtain the ξ expansion of \mathcal{Z} to second order, $\mathcal{Z} \simeq \mathcal{Z}_0 + \xi \mathcal{Z}_1 + \frac{1}{2}\xi^2 \mathcal{Z}_2$, and the linear susceptibility will simply follow as a combination of the expansion coefficients:

$$\chi = \beta \left[\frac{\mathcal{Z}''}{\mathcal{Z}} - \left(\frac{\mathcal{Z}'}{\mathcal{Z}} \right)^2 \right] \Big|_{\xi=0} = \beta \left[\frac{\mathcal{Z}_2}{\mathcal{Z}_0} - \left(\frac{\mathcal{Z}_1}{\mathcal{Z}_0} \right)^2 \right]. \quad (2.6)$$

2.2. Perturbative treatment

When one proceeds to expand the partition function

$$\mathcal{Z} = \text{Tr} e^{-\beta(\mathcal{H}_0 + V)}, \quad V = -fQ, \quad (2.7)$$

with respect to $\xi = \beta f$, one faces the problem of handling exponentials of operators or matrices. Classically, one proceeds by factorizing and expanding $e^{a+b} = e^a e^b \simeq e^a (1 + b + b^2/2 + \dots)$. For operators, however, plain factorization does not hold and one has instead a Baker–Campbell–Hausdorff formula:

$$e^{A+B} = e^A e^B e^{-\frac{1}{2}[A,B]} e^{+\frac{1}{6}([A,[A,B]] + [B,[A,B]])} \dots \quad (2.8)$$

This kind of expression is useful if one can recurrently write higher-order commutators, e.g. $[A, [A, B]]$, in terms of lower-order ones, $A, B, [A, B]$. For example, when $A \sim S_z$ and $B \sim S_\pm = S_x \pm iS_y$ (isotropic spin), or when $A \sim b_+ b_-$ and $B \sim b_\pm$, with $[b_-, b_+] = \mathbb{I}$ (harmonic oscillators). But in the general case equation (2.8) is of little use to do perturbation theory in one of the operators (actually, already for $A \sim S_z^2$ and $B \sim S_\pm$).

⁵ The proof of (2.4) is a bit less direct than it looks, because one cannot differentiate the exponential of a matrix plainly as $\partial_\xi e^{A(\xi)} \neq e^{A(\xi)} \partial_\xi A$, when A and $\partial_\xi A$ do not commute. However, using the proper identity $\partial_\xi e^{A(\xi)} = \int_0^1 d\sigma e^{(1-\sigma)A(\xi)} (\partial_\xi A) e^{+\sigma A(\xi)}$, with σ an auxiliary parameter, along with the cyclic property of the trace $\text{Tr}(CD) = \text{Tr}(DC)$, one arrives at the desired result: $\partial_\xi \text{Tr} e^{A(\xi)} = \text{Tr}(e^A \partial_\xi A)$, with the trace removing any ordering problem.

2.2.1. Perturbations from a Kubo identity (interaction picture). A way out in the problem of handling operator exponentials is provided by Kubo identities of the type [27, page 148]

$$e^{A+B} = e^A \left[\mathbb{I} + \int_0^1 d\sigma e^{-\sigma A} B e^{+\sigma(A+B)} \right], \quad (2.9)$$

where one resorts to an integral over an auxiliary parameter⁶. The integrand includes B (now freed) and again the exponential of the sum. Therefore, by iterating the same expression, $e^{\sigma(A+B)} = e^{\sigma A} [\mathbb{I} + \int_0^\sigma d\tau e^{-\tau A} B e^{+\tau(A+B)}]$ one generates the successive powers of B and can do perturbation theory.

For example, to get second-order derivatives of \mathcal{Z} , one just needs to iterate to second order. Then the B in the last $e^{+\tau(A+B)}$ is dropped (as there are already two B multiplying it), and one is left with

$$e^{A+B} \simeq e^A \left[\mathbb{I} + \int_0^1 d\sigma \overbrace{e^{-\sigma A} B e^{+\sigma A}} + \int_0^1 d\sigma e^{-\sigma A} B e^{+\sigma A} \int_0^\sigma d\tau e^{-\tau A} B e^{+\tau A} \right]. \quad (2.10)$$

Here we recognize the ‘interaction-picture’ evolution $e^{-\sigma A} B e^{+\sigma A}$. Indeed the structure of the above formula is present in most of quantum-mechanical perturbation theory [33], including scattering; it is also used to derive weak-coupling master equations in quantum open systems [27, 34].

2.2.2. Tracing and the Kubo correlator. Tracing is now required to get $\mathcal{Z} = \text{Tr} e^{-\beta\mathcal{H}}$. The trace will simplify the perturbative treatment (as compared with perturbed time evolutions) by allowing us to move operators around in combinations like $e^{-\sigma A} B e^{+\sigma A}$, using the trace’s cyclic property. We will undertake this first, arriving at the structure of the *Kubo correlator* [35], and then simplify further by doing the trace in the eigenbasis of A .

(i) *Simplifying the trace by cycling.* Using $\text{Tr}(CD) = \text{Tr}(DC)$ when tracing the second term in (2.10) one gets rid of the integral, as the first exponential can be moved to the end, canceling the dependence on the auxiliary variable σ . The third term also simplifies, following a procedure explained in most field-theory books⁷. Collecting the results one arrives at

$$\begin{aligned} \text{Tr}(e^{A+B}) &\simeq \text{Tr}(e^A) + \text{Tr}(e^A B) \\ &+ \frac{1}{2} \int_0^1 d\sigma \text{Tr}[e^{(1-\sigma)A} B e^{+\sigma A} B]. \end{aligned} \quad (2.11)$$

⁶ The same kind of auxiliary parameter, with in principle no physical meaning, we used to handle $\partial_\xi e^{A(\xi)}$. The proof of equation (2.9) follows in four simple steps: (i) isolate the integral by left-multiplying by e^{-A} . (ii) Define $F(\lambda) := e^{-\lambda A} e^{+\lambda(A+B)}$; then $F(0) = \mathbb{I}$, while $F(1)$ is the target. (iii) Differentiate with respect to λ (no ordering problems) to get $F'(\lambda) = e^{-\lambda A} B e^{+\lambda(A+B)}$; we are almost done (cf the integrand in equation (2.9)). (iv) Integral reconstruction $F(1) = F(0) + \int_0^1 d\sigma F'(\sigma)$ gives the $[\mathbb{I} + \int_0^1 \dots]$ on the right-hand side of (2.9).

⁷ See, for example, [36, chapter 8.3]. One first converts the integral over the triangle $\sigma \in [0, 1] \tau \in [0, \sigma]$ into the integral over the unit square $[0, 1] \times [0, 1]$ by using ‘chronological’ ordering (this yields a factor 1/2). Then the cyclic property of the trace is used to show that the integrand does not depend on one of the integration parameters.

We see that one of the auxiliary parameters, σ , is still with us; indeed the last term is a bare form of the Kubo correlator, $\int_0^\beta d\sigma \text{Tr}[e^{(\beta-\sigma)\mathcal{H}_0} V e^{+\sigma\mathcal{H}_0} V]$.

The goal is therefore accomplished: tracing the exponential of a sum of operators to second order in one of them. For this, Baker–Campbell–Hausdorff is not suited, while a classical handling of the operators $e^{A+B} \simeq e^A(1+B+B^2/2)$, would give correct results only to first order.

(ii) *Tracing in the unperturbed eigenbasis.* When the eigenstructure of the operator A is known, $A|m\rangle = a_m|m\rangle$, the trace can be written explicitly in terms of the eigenvalues a_m and the matrix elements of the perturbation:

$$A|m\rangle = a_m|m\rangle \quad B_{mn} = \langle m|B|n\rangle. \quad (2.12)$$

Indeed, sandwiching identities $\mathbb{I} = \sum_n |n\rangle\langle n|$ between e^A and B , the three parts of equation (2.11) give

$$\begin{aligned} \text{Tr}(e^A) &= \sum_m e^{a_m}, & \text{Tr}(e^A B) &= \sum_m e^{a_m} B_{mm} \\ \frac{1}{2} \int_0^1 d\sigma \text{Tr}[e^{(1-\sigma)A} B e^{+\sigma A} B] & & (2.13) \\ &= \frac{1}{2} \sum_{mn} e^{a_m} |B_{mn}|^2 K(a_n - a_m), \end{aligned}$$

where we have written $B_{mn}B_{nm} = |B_{mn}|^2$ for Hermitian B . The integral over σ produced the Kubo function:

$$K(X) := \int_0^1 d\sigma e^{\sigma X} = (e^X - 1)/X, \quad (2.14)$$

which enters evaluated at all eigenvalue differences $X = a_n - a_m$. This function will follow us all the way to the final expressions⁸.

2.2.3. *Application to the original perturbative problem.* Let us write down the explicit correspondence with our original perturbative trace problem $\mathcal{Z} = \text{Tr} \exp[-\beta(\mathcal{H}_0 - fQ)]$:

$$-\beta\mathcal{H} = \underbrace{-\beta\mathcal{H}_0}_A + \underbrace{\xi Q}_B. \quad (2.15)$$

Now the unperturbed eigenstructure is

$$\mathcal{H}_0|m\rangle = \varepsilon_m|m\rangle \rightsquigarrow a_m = -\beta\varepsilon_m \quad B_{mn} = \xi Q_{mn}. \quad (2.16)$$

Then comparison of equations (2.11) and (2.13) with the ξ expansion of $\mathcal{Z} \simeq \mathcal{Z}_0 + \xi\mathcal{Z}_1 + \frac{1}{2}\xi^2\mathcal{Z}_2$, gives the sought-for coefficients

$$\begin{aligned} \mathcal{Z}_0 &= \sum_m e^{-\beta\varepsilon_m}, & \mathcal{Z}_1 &= \sum_m e^{-\beta\varepsilon_m} Q_{mm}, \\ \mathcal{Z}_2 &= \sum_{mn} e^{-\beta\varepsilon_m} |Q_{mn}|^2 K_{mn}. \end{aligned} \quad (2.17)$$

⁸ Note the connection $K(X) = 1/W_1(X)$, with $W_k(X) = X^k/(e^X - 1)$ a transition rate from the theory of open quantum systems ($k = 1$ corresponds to an ‘ohmic’ bath [15, 34]). Thus, the Kubo function enjoys a ‘detailed-balance’ relation as well: $K(-X) = e^{-X} K(X)$, useful in some manipulations.

In the last term we have introduced the shorthand

$$K_{mn} := K[\beta(\varepsilon_m - \varepsilon_n)] =: K(\beta\Delta_{mn}), \quad (2.18)$$

with the Kubo function evaluated at the level differences $\Delta_{mn} := \varepsilon_m - \varepsilon_n$ (‘transition’ frequencies).

(i) *Absence of small-denominator problems.* A final remark now on perturbation theory with close levels. If we combine the denominator $\varepsilon_m - \varepsilon_n$ from K_{mn} with the matrix element $|Q_{mn}|^2$, one actually sees the structure of plain quantum-mechanical perturbation theory: $Q_{mn}Q_{nm}/(\varepsilon_m - \varepsilon_n)$. However, there is no need to handle degenerate levels, if they exist, in a special way (i.e. no need of pairing, etc [31]). The formalism ensures that the *finite temperature* perturbative treatment is finite as well. Indeed, the Taylor expansion of $K(X) = (e^X - 1)/X$:

$$K(X) \simeq 1 + X/2 + X^2/6 + \dots, \quad (2.19)$$

shows that degenerate levels $\Delta_{mn} = 0$ would contribute a finite $K(0) = 1$. This property spares us with a degenerate perturbation theory to handle close levels $\varepsilon_m \simeq \varepsilon_n$, and is built in the finite temperature formalism (to second order at least).

2.3. Formulae for the susceptibility

Now it is immediate to write down explicit expressions for the susceptibility, by plugging the \mathcal{Z} expansion coefficients (2.17) into $\chi = \beta[(\mathcal{Z}_2/\mathcal{Z}_0) - (\mathcal{Z}_1/\mathcal{Z}_0)^2]$. This form is generic for what we called ‘response observables’ in section 2.1.1, that is $\chi = \partial_f \langle Q \rangle$ with $Q = -\partial_f \mathcal{H}$, as in the examples of a coordinate, $-F x$, a spin component, $-B_z S_z$, etc.

In what follows we will address the structure of the resulting susceptibilities, and then particularize the discussion to ‘ladder perturbations’, which include simple mechanical oscillators and uniaxial paramagnets.

2.3.1. *General χ at zero bias.* As a quick illustration, in the unbiased case where $F = 0$ or $B_z = 0$, one has $\mathcal{Z}_1 = 0$ as well, and the susceptibility simply is (we will restore $\mathcal{Z}_1 \neq 0$ shortly)

$$\chi = \frac{\beta}{\mathcal{Z}_0} \sum_{mn} e^{-\beta\varepsilon_m} |Q_{mn}|^2 K_{mn}. \quad (2.20)$$

This is the kind of ready-to-use expression we mentioned in section 1. It is written fully in terms of the unperturbed eigenstructure $\{\varepsilon_m, |m\rangle\}$, $Q_{mn} = \langle m|Q|n\rangle$ and $K_{mn} = K[\beta(\varepsilon_m - \varepsilon_n)]$. It looks like an average over the unperturbed system, resembling the classical result $\chi \sim \langle S_i^2 \rangle$, but with K_{mn} encoding effects of non-commutativity of the perturbation Q and the base Hamiltonian. With simple numerical diagonalization, the χ above can be used for a nonlinear oscillator, $\mathcal{H}_0 \sim -\frac{1}{2}k x^2 + \frac{1}{4}q x^4$, or arbitrary anisotropic spins, $\mathcal{H}_0 \sim -DS_{z,\pm}^2 - K S_{z,\pm}^4 \dots$, with $S_\pm = S_x \pm iS_y$, (in particular biaxial systems).

2.3.2. χ for ladder perturbations (harmonic oscillators and uniaxial magnets). The general expression for the susceptibility obtained by plugging the \mathcal{Z}_i from equation (2.17) into $\chi = \beta[(\mathcal{Z}_2/\mathcal{Z}_0) - (\mathcal{Z}_1/\mathcal{Z}_0)^2]$ simplifies when the coupled observable Q gives, at most, transitions to adjacent levels: $m \rightarrow m$ and $m \rightarrow m \pm 1$. Then one can write

$$Q = \hat{b} \cdot \vec{S} = b_0 S_0 + \frac{1}{2}(b_+ S_- + b_- S_+), \quad (2.21)$$

with the following action on the unperturbed basis:

$$S_0|m\rangle = \ell_m^0|m\rangle \quad S_{\pm}|m\rangle = \ell_m^{\pm}|m \pm 1\rangle. \quad (2.22)$$

The harmonic oscillator corresponds to no central term $\ell_m^0 = 0$ and the creation–destruction factors $\ell_m^{\pm} = [(m + \frac{1}{2}) \pm \frac{1}{2}]^{1/2}$. For spin problems, the coefficients are $\ell_m^0 = m$ and the custom angular-momentum ladder factors $\ell_m^{\pm} = \sqrt{S(S+1) - m(m \pm 1)}$.⁹

For these ‘ladder perturbations’ the terms with b_0 in $\mathcal{Z}_2/\mathcal{Z}_0$ and $(\mathcal{Z}_2/\mathcal{Z}_0)^2$ can be combined, while the ladder action (2.22) reduces the double sum \sum_{mn} to a single sum. The susceptibility then is

$$\begin{aligned} \chi &= b_0^2 \frac{\beta}{\mathcal{Z}_0} \sum_m e^{-\beta \varepsilon_m} [(\ell_m^0)^2 - \langle \ell_m^0 \rangle^2] \\ &+ \frac{1}{4} b_+ b_- \frac{\beta}{\mathcal{Z}_0} \sum_m [(\ell_m^+)^2 G_{m,m+1} + (\ell_m^-)^2 G_{m,m-1}] \end{aligned} \quad (2.23)$$

where we have temporarily introduced the shorthand $G_{m,n} = e^{-\beta \varepsilon_m} K_{mn}$. It is not difficult to check the symmetry $G_{n,m} = G_{m,n}$ from the detailed-balance property $K(-X) = e^{-X} K(X)$ mentioned above. This symmetry, together with $\ell_m^{\pm} = \ell_{m \pm 1}^{\mp}$, leads to the two sums in the transverse $b_+ b_-$ part being equal (the sums, not the summands). Therefore we can keep one of them, replacing the factor 1/4 in front by 1/2.¹⁰

2.3.3. *Final expression/summary for uniaxial magnets.* We conclude by writing explicitly χ for paramagnets with $\mathcal{H}_0 = \mathcal{H}_0(S_z)$ probed by a field $\propto -\hat{b} \cdot \vec{S}$. The unperturbed basis is then the standard basis $S_z|m\rangle = m|m\rangle$. $b_{\parallel} := b_z$ is the direction cosine of the probing field *parallel* to the magnet local axis, while $b_{\perp}^2 = b_+ b_-$ corresponds to the *transverse* one.

The susceptibility can then be decomposed into

$$\chi = b_{\parallel}^2 \chi_{\parallel} + b_{\perp}^2 \chi_{\perp}, \quad (2.24)$$

with the longitudinal and transverse components given by

$$\chi_{\parallel} = \frac{\beta}{\mathcal{Z}_0} \sum_m e^{-\beta \varepsilon_m} (m^2 - \langle m \rangle^2) \quad (2.25)$$

$$\chi_{\perp} = \frac{\beta}{2\mathcal{Z}_0} \sum_m e^{-\beta \varepsilon_m} \ell_m^2 K_m. \quad (2.26)$$

⁹ Note that here we are already thinking of an unperturbed $\mathcal{H}_0 = \mathcal{H}_0(S_z)$; otherwise the standard basis, where \vec{S} has the ladder properties (2.22), does not diagonalize \mathcal{H}_0 and we would have to resort back to the more general (2.20).

¹⁰ The equality $\sum_m (\ell_m^+)^2 G_{m,m+1} = \sum_m (\ell_m^-)^2 G_{m,m-1}$ can also be proved directly from the Kubo correlator, as those terms correspond to $\int_0^{\beta} d\sigma \text{Tr}[e^{(\beta-\sigma)\mathcal{H}_0(S_z)} S_{\pm} e^{+\sigma\mathcal{H}_0(S_z)} S_{\mp}]$.

Here $\mathcal{Z}_0 = \sum_m e^{-\beta \varepsilon_m}$ and we have done the mentioned reduction of the duplicated terms (keeping $\sum_m (\ell_m^+)^2 G_{m,m+1}$) and simplified some notation:

$$\ell_m^2 := (\ell_m^+)^2 = S(S+1) - m(m+1) \quad (2.27)$$

$$K_m := K_{m,m+1} = K(\beta \Delta_{m,m+1}). \quad (2.28)$$

Thus the Kubo function $K(X) = (e^X - 1)/X$ enters evaluated at the ‘upward’ transition frequency $\Delta_{mm+1} = \varepsilon_m - \varepsilon_{m+1}$. The rest of the paper will consist essentially of examples and applications of equations (2.25) and (2.26).

Some remarks. Before closing this section, two remarks are in order. First, the longitudinal χ_{\parallel} can be obtained directly from derivatives of the unperturbed partition function \mathcal{Z}_0 , with respect to the static field, as is well known. In our notation, when $\mathcal{H}_0 = \mathcal{H}_a(S_z) - S_z B_z$, the levels are $-\beta \varepsilon_m = -\beta \varepsilon_m^a + m y$, with the dimensionless variable $y = \beta B_z$. Then $\mathcal{Z}_0 = \sum_m e^{-\beta \varepsilon_m^a + m y}$, whence $\mathcal{Z}_0 \langle m^k \rangle = d^k \mathcal{Z}_0 / dy^k$ for any moment $\langle m^k \rangle$. As a result

$$\langle m \rangle = \frac{1}{\mathcal{Z}_0} \frac{d\mathcal{Z}_0}{dy} \quad \langle m^2 \rangle - \langle m \rangle^2 = \frac{d \langle m \rangle}{dy}, \quad (2.29)$$

from which χ_{\parallel} follows as $\chi_{\parallel} = \beta d \langle m \rangle / dy$ with $y = \beta B_z$.

The last remark is on angular behavior. The susceptibility proper is a tensor quantity χ_{ij} relating two vectors (magnetic moment and probing field). What we have been using throughout is the projected scalar form $\chi := \sum_{ij} \chi_{ij} b_i b_j = \chi_{zz} b_z^2 + \chi_{xx} (b_x^2 + b_y^2)$, where the last form holds for uniaxial symmetry. Then, for a system of non-interacting spins with a distribution of axes orientations, the scalar χ follows from the corresponding angular averages $\overline{b_{\parallel}^2}$ and $\overline{b_{\perp}^2}$. This can be done, for example, when there is no bias field singling out a preferred direction; then one has

$$\bar{\chi} = \frac{1}{3} \chi_{\parallel} + \frac{2}{3} \chi_{\perp}, \quad (2.30)$$

for the susceptibility of a system with anisotropy axes distributed at random (powder sample, liquids, etc).

3. Paramagnets

In this section we will check the formulae of section 2, particularizing them to simple paramagnets. We will consider isotropic spins $\forall S$ and anisotropic spins with $S = 1$ and $3/2$. The susceptibility for anisotropic problems is typically obtained using Van Vleck’s method, solving the eigenvalue problem in the presence of the probing field [29, 30]. We will plainly recover those standard formulae of molecular magnetism textbooks (bypassing diagonalization) and minimally extend them by including longitudinal bias fields. Here we will also see the first examples of the

$\chi(T)$ phenomenology that will be discussed later on for general S .¹¹

3.1. Isotropic spin (Brillouin χ)

This is the simplest paramagnetic problem [1, 12], with Hamiltonian $\mathcal{H}_0 = -S_z B_z$ and spectrum $-\beta\varepsilon_m = my$. The energy levels are equispaced $\beta\Delta_{mm+1} = y$, yielding a m -independent Kubo factor $K(y)$. Besides, the partition function

$$\mathcal{Z}_0 = \sum_{m=-S}^S e^{my} = \frac{\sinh[(S + \frac{1}{2})y]}{\sinh(\frac{1}{2}y)}, \quad y = B_z/T, \quad (3.1)$$

follows readily by summing the geometric series $\sum_m (e^y)^m$.

3.1.1. Longitudinal susceptibility. As discussed above, the longitudinal response follows entirely from B_z derivatives of \mathcal{Z}_0 . The first moment is the magnetization

$$\langle m \rangle = (S + \frac{1}{2}) \coth[(S + \frac{1}{2})y] - \frac{1}{2} \coth(\frac{1}{2}y), \quad (3.2)$$

with the right-hand side defining the Brillouin function. One further derivative, using $(\coth x)' = 1 - \coth^2 x$, gives the susceptibility $\chi_{\parallel} = \beta d\langle m \rangle / dy$ as

$$\chi_{\parallel} = \beta S(S + 1) - \beta[(S + \frac{1}{2})^2 \coth^2[(S + \frac{1}{2})y] - \frac{1}{4} \coth^2(\frac{1}{2}y)]. \quad (3.3)$$

In the weak-field limit, one can use $\coth^2 x \simeq 1/x^2 + 2/3$ to show that χ_{\parallel} duly reduces to the *Curie law*:

$$\chi_{\parallel} \xrightarrow{y \rightarrow 0} \chi_c = \frac{1}{3} \beta S(S + 1). \quad (3.4)$$

This famous $1/T$ dependence was found experimentally by Pierre Curie in 1895 [1, chapter 3] and it has been fruitfully exploited for calibration and thermometry in the low temperature world. It expresses the decrease of the response with increasing T due to the thermal misalignment of the dipole moments away from the probing field direction.

3.1.2. Transverse susceptibility. From the general equation (2.26) for χ_{\perp} , plus the equispaced $-\beta\varepsilon_m = my$ for isotropic spins, one forms

$$\chi_{\perp} = \frac{\beta}{2} \sum_m \frac{e^{my}}{\mathcal{Z}_0} \ell_m^2 K(y). \quad (3.5)$$

The m -independent Kubo term $K(y) = (e^y - 1)/y$ can be taken out of the sum, which can be done explicitly:

$$\sum_m \frac{e^{my}}{\mathcal{Z}_0} [S(S + 1) - m(m + 1)] = [\coth(\frac{1}{2}y) - 1] \langle m \rangle. \quad (3.6)$$

¹¹ The reader may well wonder why we have not used Bose/Fermi statistics for integer/half-integer S . First, the only basic statistics is Gibbs-Boltzmann, with Bose/Fermi distributions as particular/worked cases of $\varrho \propto e^{-\beta\mathcal{H}}$ for the ideal gas of *indistinguishable* bosons or fermions. But we implicitly bypass indistinguishability by locating/labeling each spin at a given lattice point (localized moments' magnetism) [1, chapter 3.1] [12, chapter 1.2]. This is the same approximation routinely used in solid state physics and quantum chemistry, where one does not symmetrize/antisymmetrize the states with respect to the nuclei exchange; an approximation grounded on the non-overlapping of the ions' wavefunctions for sufficiently localized states.

But the square bracket can be written as $2/(e^y - 1)$, which combined with the Kubo factor leaves the simple form $\chi_{\perp} = (\beta/y)\langle m \rangle$. That is (recall $y = \beta B_z$):

$$\chi_{\perp} = \frac{\langle m \rangle}{B_z} \xrightarrow{y \rightarrow 0} \frac{1}{3} \beta S(S + 1), \quad (3.7)$$

which also recovers the correct Curie limit at low fields, as expected from the restoration of isotropy¹².

It is important to remark that χ_{\perp} does not follow from the transverse fluctuations of the spin, as one might naively expect. Indeed, using $S_x^2 + S_y^2 = S(S + 1) - S_z^2$ one gets for $\mathcal{H}_0 = -S_z B_z$

$$\beta \langle S_x^2 \rangle = \beta \langle S_y^2 \rangle = \frac{1}{2} y \coth\left(\frac{1}{2}y\right) \times \frac{\langle m \rangle}{B_z} \neq \chi_{\perp}. \quad (3.8)$$

They only agree at high temperature, $y = \beta B_z \ll 1$, where the extra pre-factor $\frac{1}{2}y \coth(\frac{1}{2}y) \rightarrow 1$. However, at low temperature, $\chi_{\perp} \rightarrow S/B_z$ (following saturation of the magnetization $\langle m \rangle \rightarrow S$), whereas $\beta \langle S_x^2 \rangle \rightarrow S/2T$, which can grow without bound as $T \rightarrow 0$. Two different behaviors indeed¹³.

3.2. Anisotropic spins

When a paramagnetic ion is embedded in a molecule or a solid, the spin finds preferred orientations which depend on the symmetries of its neighborhood. This magnetic anisotropy can be described by adding to the spin Hamiltonian a term $\mathcal{H}_a(\vec{S})$ with 'reflection' symmetry $\mathcal{H}_a(-\vec{S}) = \mathcal{H}_a(\vec{S})$ (to respect time-reversal invariance). The simplest model is the uniaxial Hamiltonian:

$$\mathcal{H}_0 = -DS_z^2 - S_z B_z, \quad (3.9)$$

with D the anisotropy constant. To do statistical mechanics we introduce the dimensionless $d = D/T$ and $y = B_z/T$ and write $-\beta\varepsilon_m = dm^2 + ym$.

The minimal mathematical extension from linear to quadratic in \vec{S} has important consequences. First, the spectrum $\varepsilon_m = -Dm^2 - B_z m$ can have a single well ($D < 0$, 'easy-plane' anisotropy) or it can display a bistable structure ($D > 0$, 'easy axis'; see figure 1). Second, the energy levels are no longer equispaced, $\Delta_{mm+1} = D(2m + 1) + B_z$, becoming closer near $m = 0$ (no 'harmonic oscillator' equispaced simplicity). In dynamics this gives a multiplicity of precession frequencies (absorption peaks), tunnel splittings and relaxation rates [12, 18, 37, 38]. But already in the statics we will find a m -dependent Kubo factor $K(\beta\Delta_{mm+1})$, expressing that $e^{-\sigma S_z^2} S_{\pm} e^{+\sigma S_z^2}$ cannot be written in terms of S_{\pm} only (another reason underlying the simplicity of isotropic spins). Finally,

¹² For $S = 1/2$ (the two-level system), one has $\langle m \rangle = \frac{1}{2} \tanh(\frac{1}{2}y)$ (population difference), so that $\chi_{\parallel} = \frac{1}{4} \beta / \cosh^2(\frac{1}{2}y)$, while $\chi_{\perp} = \tanh(\frac{1}{2}y)/2B_z$. Both duly give $\chi_c = \frac{1}{4} \beta$ at zero field ($S(S + 1) = 1/4$). In the opposite, classical limit $S \gg 1$, one has $\chi_{\parallel} = \beta \mu^2 L(\xi)$ and $\chi_{\perp} = (\mu/B_z)L(\xi)$ for isotropic superparamagnets, with the Langevin magnetization $L(\xi) = \coth \xi - 1/\xi$ and $\xi = \mu B_z/T$; see, for instance, [9, equation (3.74)].

¹³ The unbounded $\beta \langle S_x^2 \rangle$ can be seen as due to 'zero-point fluctuations', since $S_x^2 + S_y^2 \rightarrow S(S + 1) - S_z^2 = S$ is different from zero even for 'fully aligned' $S_z \rightarrow S$; the actual χ_{\perp} corrects for this and leaves the response induced by the probing field.

the partition function $\mathcal{Z}_0 = \sum_m e^{dm^2+ym}$, with $d = D/T$ and $y = B_z/T$, cannot be summed explicitly (Gauss-type sums), though simple formulae can be produced for small S .¹⁴

3.2.1. Susceptibilities for $S = 1$. Spin 1 is the first case giving new phenomenology; in the case $S = 1/2$ the term $-DS_z^2$ produces a uniform level shift, so that χ is the same as that of the isotropic $S = 1/2$ spin discussed above.

For $S = 1$ at zero field, there are two facing energy levels $m = \pm 1$ (minima for $D > 0$) with the level $m = 0$ in between (a maximum or minimum, depending on the sign of D ; top left panel in figure 1). In table 1 we have collected the energy levels, ladder factors and transition frequencies required to calculate the equilibrium response. In terms of $d = D/T$ and $y = B_z/T$, the partition function (2.2) is

$$\mathcal{Z}_0 = 1 + 2e^d \cosh y, \quad (S = 1), \quad (3.10)$$

which enters in both χ_{\parallel} and χ_{\perp} .

(i) *Longitudinal susceptibility $\chi_{\parallel}(S = 1)$.* Differentiating \mathcal{Z}_0 one gets the magnetization $\langle m \rangle = \mathcal{Z}_0^{-1} d\mathcal{Z}_0/dy$, which can be cast in the suggestive form

$$\langle m \rangle = \frac{\sinh y}{\cosh y + \frac{1}{2}e^{-d}}. \quad (3.11)$$

The $m = 0$ level does not contribute to the numerator $\sum m e^{-\beta\epsilon_m}$ but occupies a ‘phase space’ $\frac{1}{2}e^{-d}$. When for $d \gg 1$ the level $m = 0$ gets thermally depopulated, and one recovers $\langle m \rangle \simeq \tanh y$, as in a two-level system.

Differentiating $\langle m \rangle$ gives the fluctuations $\langle m^2 \rangle - \langle m \rangle^2 = d\langle m \rangle/dy$, which multiplied by $\beta = 1/T$ gives the longitudinal susceptibility:

$$\chi_{\parallel} = \beta \frac{1 + \frac{1}{2}e^{-d} \cosh y}{(\cosh y + \frac{1}{2}e^{-d})^2}, \quad (S = 1). \quad (3.12)$$

Again, $d \gg 1$ leads to the two-level type susceptibility $\chi_{\parallel} \simeq \beta/\cosh^2 y$.

(ii) *Transverse susceptibility $\chi_{\perp}(S = 1)$.* Picking from table 1, plugging in equation (2.26) and playing with $K(-X) = e^{-X}K(X)$, we can write the transverse response as $\chi_{\perp} = (\beta/\mathcal{Z}_0)[K(d-y) + K(d+y)]$. Alternatively, we can unfold the Kubo functions and use $(d \pm y)/\beta = D \pm B_z$, obtaining

$$\chi_{\perp} = \frac{1}{\mathcal{Z}_0} \left[\frac{e^{d-y} - 1}{D - B_z} + \frac{e^{d+y} - 1}{D + B_z} \right], \quad (S = 1). \quad (3.13)$$

¹⁴ Slow dynamics at low T is an important consequence of the anisotropy. From the point of view of the many relaxation rates [37, 38], one of the rates is well separated from the others (the analog of the lowest non-vanishing eigenvalue in the framework of the Fokker–Planck equation). The faster rates correspond to intrawell modes, while the slow mode is associated with the overbarrier dynamics of the spin; due to thermal activation it is suppressed exponentially at low T by $\exp(-\Delta U/T)$. The phenomenological ‘blocking temperature’ is that where the observational time window t_m matches this slow dynamics; below it, the given technique does not ‘record’ any more equilibrium properties.

Table 1. Energy levels $-\beta\epsilon_m = dm^2 + ym$, ladder factors $\ell_m^2 = 2 - m(m+1)$ and transition frequencies $\beta\Delta_{mm+1} = \beta(\epsilon_m - \epsilon_{m+1}) = d(2m+1) + y$, for $S = 1$. Note $S(S+1) = 2$ and $\frac{1}{3}S(S+1) = 2/3$.

m	$-\beta\epsilon_m$	ℓ_m^2	$\beta\Delta_{mm+1}$
-1	$d - y$	2	$-d + y$
0	0	2	$+d + y$
+1	$d + y$	0	—

As mentioned before, χ_{\perp} remains finite when adjacent levels become degenerate (e.g. when $B_z = \pm D$). Note finally that when $d \rightarrow 0$, we have

$$\chi_{\perp} \simeq \frac{1}{B_z} \frac{\sinh y}{\cosh y + \frac{1}{2}} = \frac{\langle m \rangle|_{S=1}}{B_z}, \quad (3.14)$$

duly recovering the transverse susceptibility (3.7) for isotropic $S = 1$ spins.

(iii) *T dependence of χ_{\parallel} and χ_{\perp} for $S = 1$.* We will set $B_z = 0$ to describe briefly the features of the T -dependent susceptibility. The above expressions, equations (3.12) and (3.13), then reduce to (cf [29, equation (2.9)])

$$\chi_{\parallel} = \frac{2}{T} \frac{1}{2 + e^{-D/T}}, \quad \chi_{\perp} = \frac{2}{D} \frac{1 - e^{-D/T}}{2 + e^{-D/T}}. \quad (3.15)$$

These susceptibilities are plotted in figure 2. At high temperature both go over the Curie curve $\chi_c = S(S+1)/3T$. This can be seen from the formulae too, as $|D/T| \ll 1$ yields $\chi_{\parallel} \simeq 2/3T$ and $\chi_{\perp} \simeq 2/3T$ (now $S(S+1) = 2$). As the temperature decreases, χ_{\perp} shows no peaks and tends to the constant response $\chi_{\perp} = 1/D$ (the analog to the classical torque susceptibility $\chi_{\perp} \sim \frac{1}{2}\partial_\theta^2 E$ [2]). The longitudinal response, on the other hand, goes over the two-state asymptote $\chi_{\parallel} \simeq 1/T = S^2/T$ at low temperatures. Therefore, as $S^2 > S(S+1)/3$, the increase of χ_{\parallel} is faster than $1/T$ in the intermediate range.

We mentioned the routine use of $\chi(T)$ curves as a characterization tool [32]. For instance, deviations from $1/T$ laws can indicate spin–spin interactions (think of the mean field $\chi \sim 1/(T - \theta)$ when observed over a short T interval). However, one should be careful with not overlooking other possible sources of deviation, such as those due to the anisotropy just discussed.

3.2.2. Susceptibilities for $S = 3/2$. We move on to the next spin value. The anisotropy term $-DS_z^2$ gives two pairs of degenerate levels without a central maximum or minimum (see figure 1, top right). The pair $|m| = 3/2$ is above or below the pair $|m| = 1/2$ depending on the sign of the anisotropy constant D .

We have put up in table 2 the relevant quantities to calculate the susceptibilities of this four-level system. From there we first compose the partition function ($d = \beta D$, $y = \beta B_z$):

$$\mathcal{Z}_0 = 2[\cosh(y/2) + e^{2d} \cosh(3y/2)], \quad (S = 3/2), \quad (3.16)$$

which will be needed in both the longitudinal and in the transverse response.

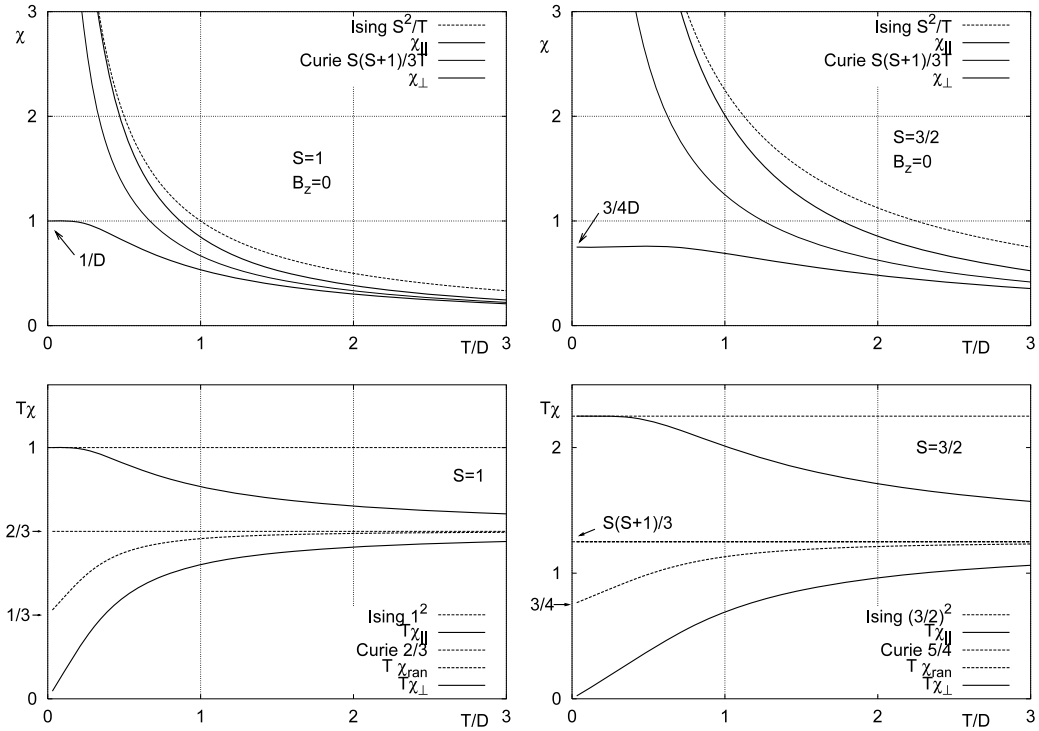


Figure 2. Susceptibilities versus temperature of spins $S = 1$ (left panels) and $S = 3/2$ (right) with easy-axis anisotropy $D = 1$ (see the spectra in figure 1). Top panels: longitudinal and transverse susceptibility versus T . The Curie law $S(S + 1)/3T$ (thin solid lines) is approached by both χ_{\parallel} and χ_{\perp} at high T . At low temperature χ_{\parallel} goes over the two-state behavior S^2/T (dashed thin lines). The transverse susceptibility tends to the constant $\chi_{\perp} = 1/[2D(1 - 1/2S)]$ at low T (equation (4.8)). Bottom panel: susceptibilities plotted as $T\chi$, including the average for axes distributed at random, $\bar{\chi} = \frac{1}{3}\chi_{\parallel} + \frac{2}{3}\chi_{\perp}$, which shows deviation from isotropy at lower temperatures.

Table 2. $S = 3/2$ energy levels $-\beta\varepsilon_m = dm^2 + ym$, ladder factors $\ell_m^2 = 15/4 - m(m + 1)$ and transition frequencies $\beta\Delta_{mm+1} = \beta(\varepsilon_m - \varepsilon_{m+1}) = d(2m + 1) + y$. Here $S(S + 1) = 15/4$ and $\frac{1}{3}S(S + 1) = 5/4$, and to spare exponentials we have shifted all energies by $d(1/2)^2$, that is $\beta\bar{\varepsilon}_m := \beta\varepsilon_m + d/4$.

m	$-\beta\bar{\varepsilon}_m$	ℓ_m^2	$\beta\Delta_{mm+1}$
$-3/2$	$2d - 3y/2$	3	$-2d + y$
$-1/2$	$-y/2$	4	$+y$
$+1/2$	$+y/2$	3	$+2d + y$
$+3/2$	$2d + 3y/2$	0	—

(i) *Longitudinal* $\chi_{\parallel}(S = 3/2)$. The y derivative of the above \mathcal{Z}_0 produces the magnetization

$$\langle m \rangle = \frac{1 \sinh(y/2) + 3 e^{2d} \sinh(3y/2)}{2 \cosh(y/2) + e^{2d} \cosh(3y/2)}. \quad (3.17)$$

As a check, one finds at low T two different two-level type responses, depending on the sign of d , namely, $\langle m \rangle \simeq (3/2) \tanh(3y/2)$ for positive D and $\langle m \rangle \simeq (1/2) \tanh(y/2)$ for negative, with the right spin values $3/2$ and $1/2$, respectively.

One more derivative gives the longitudinal fluctuations entering in the susceptibility $\chi_{\parallel} = \beta \langle m^2 \rangle - \langle m \rangle^2$:

$$\chi_{\parallel} = \frac{\beta}{4} \frac{1 + 2 e^{2d} (4 \cosh y + \cosh 2y) + 9 e^{4d}}{[\cosh(y/2) + e^{2d} \cosh(3y/2)]^2}. \quad (3.18)$$

Consistent with the above magnetizations, $d \gg 1$ gives $\chi_{\parallel} \simeq \beta(3/2)^2 / \cosh^2(3y/2)$ while $d \ll -1$ yields $\chi_{\parallel} \simeq \beta(1/2)^2 / \cosh^2(y/2)$ as low temperature two-level asymptotics.

(ii) *Transverse* $\chi_{\perp}(S = 3/2)$. We next assemble the transverse susceptibility from the quantities of table 2:

$$\chi_{\perp} = \frac{\beta}{2\mathcal{Z}_0} [3e^{-y/2} K(2d - y) + 4e^{-y/2} K(+y) + 3e^{+y/2} K(2d + y)], \quad (S = 3/2). \quad (3.19)$$

with the custom $K(X) = (e^X - 1)/X$. We have played again with the detailed-balance property $K(-X) = e^{-X} K(X)$ to arrive at a compact form (e.g. note that the middle term is either $e^{-y/2} K(+y) = e^{+y/2} K(-y) = \sinh(y/2)/(y/2)$).

(iii) *Temperature dependence of χ_{\parallel} and χ_{\perp} for $S = 3/2$* . In the unbiased $B_z = 0$ case, equations (3.18) and (3.19) reduce to

$$\chi_{\parallel} = \frac{\beta}{4} \frac{e^{-2d} + 10 + 9e^{+2d}}{4 \cosh^2 d}, \quad (3.20)$$

$$\chi_{\perp} = \frac{\beta}{2(1 + e^{2d})} [3K(2d) + 2].$$

Both approach the Curie curve $\chi_c = 5/4T$ when $d = D/T \rightarrow 0$, as seen in the high temperature range of figure 2 (now $S(S + 1) = 15/4$). Again, at low temperature χ_{\parallel} has to catch up with the two-level asymptote $\chi_{\parallel} \simeq S^2/T$ (with $S = 3/2$ for $D > 0$), increasing faster than $1/T$ in the crossover range.

The transverse χ_{\perp} tends to a constant value as $T \rightarrow 0$, but it displays a small and broad maximum around $T \sim D/2$, which was absent in $S = 1$ (and hardly visible here). The maximum can be obtained from the alternative form $\chi_{\perp} = \frac{3}{4D} [\tanh d + \frac{2}{3}d(1 - \tanh d)]$, where $d(1 - \tanh d)$ adds a small bump to the monotonic $\tanh d$ as T decreases ($d = D/T$).

We close with the susceptibility for the ensemble with anisotropy axes oriented at random. Figure 2 shows that $\bar{\chi} = \frac{1}{3}\chi_{\parallel} + \frac{2}{3}\chi_{\perp}$ matches the isotropic Curie curve over a wider T range than χ_{\parallel} and χ_{\perp} ; actually down to $T \sim D-2D$, where it eventually deviates downwards. This behavior was also shown by $S = 1$ and will be addressed in section 4 for larger S values.

4. Superparamagnets

Discussing the T dependence of the susceptibility of anisotropic spins $S = 1$ and $3/2$ we have come across some features of the curves that we would like to study more systematically, for several S . We want to check if those behaviors are specific of some spin values, how they evolve with S and whether they survive the classical/continuum limit $S \rightarrow \infty$.

We have in mind three features: (1) the crossover of χ_{\parallel} from the Curie law $\chi_c = \frac{1}{3}\beta S(S+1)$ toward the two-state response as T is lowered, (2) the peak in the transverse $\chi_{\perp}(T)$ around the anisotropy constant D and (3) the deviation of the orientationally randomized $\bar{\chi}$ from Curie at low temperature¹⁵.

Technically, the study as a function of S is eased by the compact expressions of section 2. We just need an algorithm building a table like those of section 3, for a given S , and feeding the formulae for χ_{\parallel} and χ_{\perp} (equations (2.25) and (2.26)) with the entries ε_m , $\ell_m^2 = S(S+1) - m(m+1)$ and $\Delta_{mm+1} = \varepsilon_m - \varepsilon_{m+1}$.

4.1. Scaling with S

To compare results for different S meaningfully, we must specify which parameters are kept constant, or how they are scaled with S . The same applies to the classical limit. This kind of specification is needed in any sensible limit-taking procedure in physics (thermodynamical limits, continuum limit from mechanics, or from lattice discretizations, etc). Different specifications/scalings give different results, possibly answering different questions.

We will use the following prescription. We compare spins with different S but having the same (maximum) energy. For the spin Hamiltonian $\mathcal{H}_0 = -DS_z^2 - \vec{B} \cdot \vec{S}$, this entails keeping fixed

$$\text{scaling: } DS^2 = \text{const.} \quad BS = \text{const.}, \quad (4.1)$$

as the spin is varied. Then the energy differences between adjacent levels $\Delta \sim DS + B_z$ will decrease as $\Delta \sim 1/S$, and the levels will approach each other accordingly. In figure 1 we have shown three spins with the same anisotropy barrier $\Delta U = DS^2$ but different numbers of levels (3, 5 and 9). Therefore, with this convention the

¹⁵One may think that (1) and (3) are the same, but in classical superparamagnets there is crossover in χ_{\parallel} but no deviation of $\bar{\chi}$ from Curie [39].

question we will be answering is how the number of levels, as a measure of discreteness/quantumness, would affect the properties observed.

In the rest of this section we will address the three points mentioned for the uniaxial model $\mathcal{H}_0 = -DS_z^2 - B_z S_z$. Having in mind actual superparamagnets, we use $D > 0$ and set $B_z = 0$ for simplicity. The quantity DS^2 , being fixed, provides a natural scale of temperature T/DS^2 , with $DS^2 \sim 10^2 - 10^3$ K in many superparamagnets [5, 10]. Similarly, the output susceptibility curves will be normalized as $\chi/S(S+1)$ to facilitate comparisons. For example, all curves $T\chi$ would go over $1/3$ at high T , and we can discuss how the low T behavior is modified by the discreteness of the spectrum.

4.2. Longitudinal response for various S

As already mentioned, understanding well the T dependence of the susceptibility of the paramagnetic ‘ideal gas’ is important because $\chi(T)$ curves are routinely used as indicators of spin-spin interactions, anisotropies, etc [29, 30, 32].

In section 3 we saw that, for anisotropic $S = 1$ and $3/2$, at high enough temperature, the susceptibility approaches the Curie asymptote $\chi_c = \frac{1}{3}\beta S(S+1)$, whereas in the low T range the highly anisotropic two-state regime $\chi_I = \beta S^2$ emerges (if you prefer, Heisenberg to Ising crossover). This is expected $\forall S$, because at high enough T the anisotropy term plays a minor role $e^{-\beta\varepsilon_m} \simeq 1$ and the spin effectively becomes a free (quantum) rotor. Indeed, arithmetic sums like $\sum_{k=1}^N k^2 = \frac{1}{3}N(N+1)(N+\frac{1}{2})$ give

$$\sum_{m=-S}^S m^2 e^{-\beta\varepsilon_m} \simeq \sum_{m=-S}^S m^2 = \frac{1}{3}S(S+1)(2S+1), \quad (4.2)$$

which divided by $\mathcal{Z}_0 \simeq \sum_m 1 = 2S+1$ (number of states) produces the Curie law $\chi_c = \frac{1}{3}\beta S(S+1)$, for all S . Then, as $-\beta\varepsilon_m = \beta D m^2$, the onset of deviation from isotropy can be defined as the temperature where $e^{-\beta\varepsilon_0} = 1$ and $e^{-\beta\varepsilon_S}$ (population of the ‘poles’ and the ‘equator’) start to differ appreciably. Say, by 5%, then $e^{DS^2/T} \simeq 1 + DS^2/T \sim 1.05$ gives $T/DS^2 \sim 20$. This estimate holds $\forall S$, as seen in the high- T range of figure 3.

In the opposite low T regime, we can approximate χ_{\parallel} by using the lowest levels $m = \pm S$ (effective two-state; classically only the poles populated):

$$\begin{aligned} \langle m^2 \rangle &= \frac{\sum_m e^{-\beta\varepsilon_m} m^2}{\sum_m e^{-\beta\varepsilon_m}} \simeq \frac{e^{-\beta\varepsilon_{-S}} (-S)^2 + e^{-\beta\varepsilon_S} S^2}{e^{-\beta\varepsilon_{-S}} + e^{-\beta\varepsilon_S}} \\ &= S^2 \rightsquigarrow \chi_{\parallel} \simeq \beta S^2. \end{aligned} \quad (4.3)$$

In this low T range, $T\chi_{\parallel}$ shows a plateau (figure 3) which does not bend until the next levels $\varepsilon_{\pm(S-1)}$ become appreciably populated. This suggests that leaving this ‘Ising plateau’ is governed by $T_1 := \Delta_{S,S-1} = D(2S-1)$ (the energy difference to the first excited pair). As this energy enters exponentially, the curves’ bend would be negligible at a $T \sim$ five times lower [$\exp(-x) \simeq 0$ at $x \sim 4-6$]. Indeed in our scaled units $T_1/5DS^2 = (2S-1)/5S^2 \sim 2/5S$. This gives a longer plateau the smaller S is, in agreement with the curves of figure 3. Note that, for large S , not only is the Ising regime

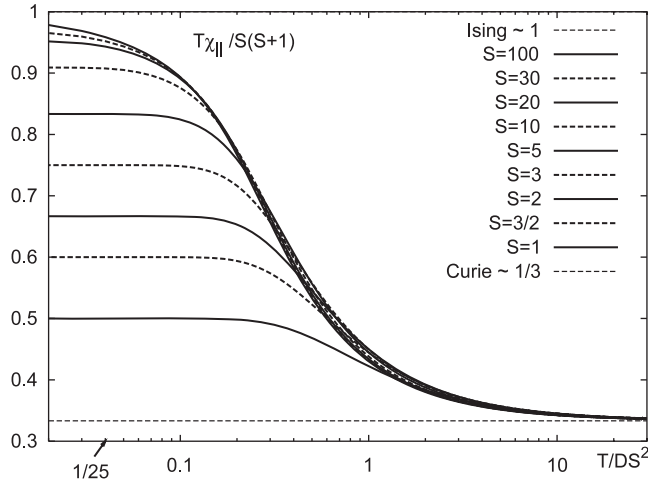


Figure 3. Longitudinal susceptibility $\chi_{||}$ versus T for several S . Curves presented as $T\chi_{||}/S(S+1)$, to show the crossover from the high- T Curie regime, $T\chi_{||}/S(S+1) = 1/3$ (thin dashed line), to the two-level regime at low temperatures. The arrow at $\sim 1/25$ indicates the lower limit of the observable equilibrium temperature window due to the onset of non-equilibrium effects (superparamagnetic blocking; cf [40]).

shorter, but it is reached more slowly when decreasing T (non-exponentially)¹⁶.

With the two estimates above we have characterized the extent of the temperature crossover for all S . As for the magnitude of the ‘excursion’, it just follows from $T\chi_{||}$ evolving from $\frac{1}{3}S(S+1)$ up to S^2 :

$$\frac{S^2}{\frac{1}{3}S(S+1)} = \frac{3S}{S+1} = \begin{cases} 3 & S \rightarrow \infty \\ 3/2 & S = 1. \end{cases} \quad (4.4)$$

This is maximum classically, 3, and decreases with S to get halved for $S = 1$. This merely reflects the familiar quantum-mechanical fact of \vec{S}^2 not having length S^2 , but $S(S+1)$.

Having characterized the crossover, one could assess the temperature ranges where approximate modelizations can be employed. For example, for classical nanoparticles the use of the Curie susceptibility is widespread (with the corresponding Langevin magnetization), unfortunately well down to the superparamagnetic blocking $T/DS^2 \sim 0.04\text{--}0.1$ (arrow in figure 3). Here we see once more that, if a rough model is to be chosen, the two-state model is preferable (with the associated $\langle m \rangle \propto \tanh(\mu B/T)$), as the pioneers of superparamagnetism properly did [4]¹⁷.

¹⁶ For classical superparamagnets $\chi_{||} = \beta\mu^2 R'/R$, where $R(\alpha) = \int_0^1 dz \exp(\alpha z^2)$ is the ‘partition function’ with $\alpha = \Delta U/T$, and $R' = dR/d\alpha$ [9, 40–44]. At low T (large α) one can approximate $R'/R \simeq 1 - 1/\alpha$, showing the non-exponential, power-law approach to $\chi_{||} \simeq \beta\mu^2$. At high T , on the other hand, letting $\alpha \rightarrow 0$ one has $R'/R = \int_0^1 dz z^2 = 1/3$, recovering the classical Curie susceptibility $\chi_{||} \simeq \frac{1}{3}\beta\mu^2$.

¹⁷ The folk view associates superparamagnetism with energy barriers $\Delta U = DS^2$ larger than T . But a crude estimate of the overbarrier relaxation time $\tau = \tau_0 \exp(\beta\Delta U)$ gives a pre-factor $\tau_0 \sim 10^{-7}\text{--}10^{-8}$ s for molecular clusters and $\tau_0 \sim 10^{-10}\text{--}10^{-12}$ s for nanoparticles [10, 5]. Superparamagnetism is to be observed for measurement times $t_m \gg \tau$. Then one can have an equilibrium/superparamagnetic temperature range as wide as $25 > \beta\Delta U \geq 0$,

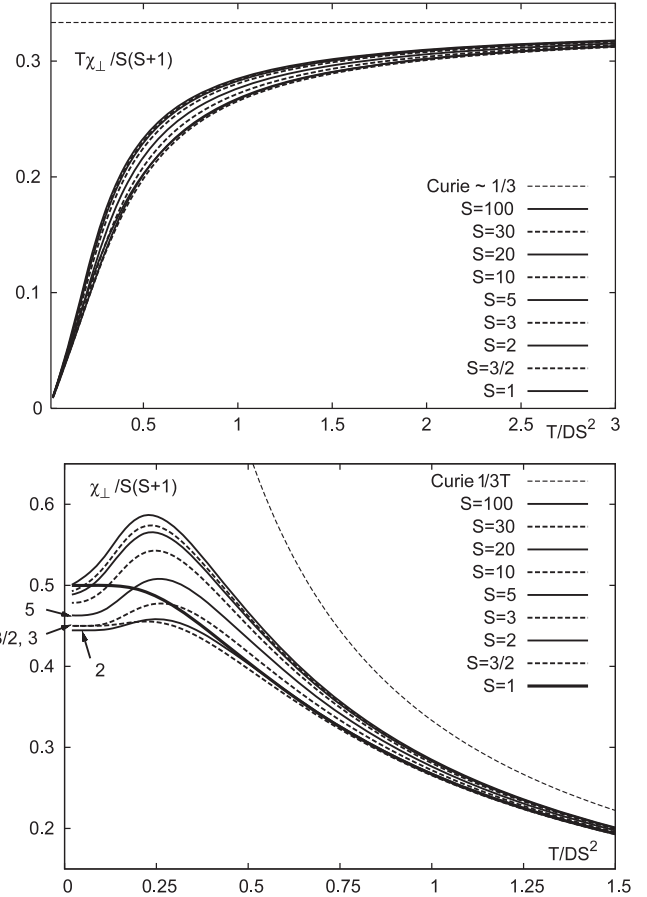


Figure 4. Upper panel: transverse susceptibility versus T for various S , plotted as $T\chi_{\perp}/S(S+1)$. The two lowest curves correspond to those of $S = 1$ and $3/2$ in figure 2. In the lower panel we plotted the raw susceptibilities, showing the peaks developed for $S \geq 3/2$, and how they evolve toward the classical curve.

4.3. Transverse susceptibility for various S

The transverse response is a process quite different from the longitudinal one. $\chi_{||}$ is about applying a small probe that shifts up and down the energy levels, and the associated repopulation involving $\exp(-\beta\Delta U)$ factors. However, a transverse probe mixes and splits the degenerate levels, and our intuition of the response gets somewhat lost.

A classical cartoon can be of some assistance. In it the effect of b_{\perp} is trying to rotate \vec{S} out of the stable anisotropy minima (the ‘up’ and ‘down’ poles) towards some point in the equator. The result of this torque can be expressed as $\chi_{\perp} \sim \frac{1}{2}\partial_{\theta}^2 E$. Thus, the transverse susceptibility is more sensitive to other features, like energy-well curvatures, rather than to barrier heights, which renders it as a valuable tool too.

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The torque picture holds at $T = 0$ (Stoner–Wohlfarth [2]), and we actually saw that, down there, χ_{\perp} tends to some constant ($\chi_{\perp} = D$ for $S = 1$ and $\chi_{\perp} = 3/4D$ for $S = 3/2$; figure 2). On the other hand, at high $T \gg D$ the anisotropy potential becomes irrelevant and one should regain

$\chi_{\perp} = \frac{1}{3}\beta S(S+1)$ once again. If we insist in a $T\chi$ plot (figure 4), this quantity will evolve from $\frac{1}{3}S(S+1)$ at high T down to 0, with an initial linear slope if $\chi_{\perp}(T)$ is nearly constant at low temperature.

This behavior is what we found before for $S = 1$ and $3/2$, i.e. for the three-level and four-level systems. But $S = 3/2$ also exhibited a small and broad maximum in $\chi_{\perp}(T)$, which is absent in $S = 1$. Is this a parity, integer/half-integer effect? Or is the absence of peak just an oddity of $S = 1$ and it persists $\forall S > 1$? The latter is suggested by the classical model having a maximum too. And indeed, plotting the bare χ_{\perp} versus T (lower panel of figure 4) we see that the peak is there for all $S > 1$, becoming more apparent for large S .¹⁸

Some interpretation can be provided combining the torque picture above with thermal activation. A small $T \neq 0$ can assist in leaving the potential minima and, on average, may help reorienting \vec{S} toward the transverse field (increasing the response). Too high a T , however, and the custom thermal misalignment would set in, decreasing the susceptibility. Then a peak in between seems natural from the competition of both processes.

Well, but why is there no peak for $S = 1$? We may answer that, lacking intermediate levels, the T that assists rotation toward $m = 0$ becomes too large and we only find the thermal decrease. Quantum mechanically it can be put in the following way. A transverse field b_x mixes the states $|m\rangle$ and $|m \pm 1\rangle$, and their contribution to $\langle S_x \rangle$ involves the factor $|\langle m+1 | S_x | m \rangle|^2 / (\varepsilon_{m+1} - \varepsilon_m) \times (e^{-\beta\varepsilon_{m+1}} - e^{-\beta\varepsilon_m})$. Then the contribution of $m = S-1$ is larger than that of $m = S$, as the above factor increases when m climbs the ladder out of $m = S$ (mostly because the levels get closer if $\varepsilon_m = -Dm^2$ so that $1/(\varepsilon_{m+1} - \varepsilon_m)$ becomes larger). However, for $S = 1$, the level $m = 0$ has no level above it providing such an increase. Then populating $m = 0$ thermally does not increase χ_{\perp} and there is no peak for spin 1.

As for the behavior of the peaks with S , we see that they move only a little in the scaled units T/DS^2 . This rules out a characteristic temperature of the type $T_0 \sim D(2S-1)$ (as invoked in the longitudinal case), because then $T_0/DS^2 \sim 1/S$, and the peak would shift left and disappear classically. We need another governing energy scale; the total barrier $\Delta U = DS^2$ would do, since it is constant in our units. Indeed, $\exp(-\Delta U/T_0) \neq 0$ would mark the onset of misalignment, as the equatorial levels then start to be populated. Using again the rule-of-thumb $\exp(-x) \simeq 0$ at $x \sim 4-6$, we would have $\Delta U/T_0 \sim 4-6$. Then $T_0/DS^2 \sim 0.16-0.25$, compatible with the peaks' location in figure 4.¹⁹

¹⁸ The initial decrease, and then increase, in $\chi_{\perp}(T=0)$ is due to our normalization and scalings (figure 4, bottom). For fixed D , the bare $\chi_{\perp}(S, T=0) = 1/[2D(1-1/2S)]$ (equation (4.8)) decreases monotonically with S : $\chi_{\perp}(1) = 1/D$, $\chi_{\perp}(3/2) = 3/4D$, $\chi_{\perp}(2) = 2/3D$, to get halved as $\chi_{\perp}(S \rightarrow \infty) = 1/2D$. But the scaling $D = 1/S^2$, plus $\chi_{\perp}/S(S+1)$, gives $\chi_{\perp} \rightarrow S^2/(2S^2 + S - 1)$, which starts from $1/2$ at $S = 1$, decreases sharply to the minimum $4/9$ at $S = 2$ and slowly returns to $1/2$ as $S \rightarrow \infty$. Notice $\chi_{\perp}(3/2) = \chi_{\perp}(3) = 0.45$ in these units.

¹⁹ In the classical model the peak can be found by plotting $\chi_{\perp} = \beta\mu^2(R - R')/2R$ [9], and is located around $T_0 \simeq 0.23$ [40]. On the other hand, the effective eigenvalue method [45] gives an effective relaxation time τ_{ef} showing a similar maximum [9, page 126]. The reason seems to be that τ_{ef} can be expressed in terms of equilibrium averages, and happens to be proportional to $1 - \langle z^2 \rangle \propto \chi_{\perp}$.

4.4. Response for randomly oriented axes

We conclude with the susceptibility of the ensemble with anisotropy axes distributed at random. This case is of experimental interest in powdered samples and liquids (ferrofluids [5]), as well as in solid systems with orientational disorders.

4.4.1. Restoring the isotropy and the classical limit. In classical superparamagnets the orientational average $\overline{b_{\parallel}^2} = 1/3$ and $\overline{b_{\perp}^2} = 2/3$ leads to a full restoration of isotropy [46, figure 1] [47]:

$$\left. \begin{aligned} \chi_{\parallel} &= \beta\mu^2 R'/R \\ \chi_{\perp} &= \beta\mu^2(R - R')/2R \end{aligned} \right\} \rightsquigarrow \bar{\chi} = \frac{1}{3}\chi_{\parallel} + \frac{2}{3}\chi_{\perp} = \frac{1}{3}\beta\mu^2. \quad (4.5)$$

That is, $R(\alpha) = \int_0^1 dz \exp(\alpha z^2)$, with $\alpha = \Delta U/T$, and its α derivative R' disappears from $\bar{\chi}$. This washing away of any trace of the anisotropy constants is not specific of the uniaxial model $\mathcal{H}_0 = -DS_z^2$, but it holds for any classical \mathcal{H}_0 with the reflection symmetry $\mathcal{H}_0(-\vec{S}) = \mathcal{H}_0(\vec{S})$ (see [39] and references therein).

Quantum mechanically, however, we know that this cannot be exact. In figure 2 we showed that for $S = 1$ and $3/2$ the random axes averaging indeed restores isotropy, $\bar{\chi} \simeq \chi_c$, over a wider temperature range. And this occurs even with χ_{\parallel} well on its way to $\chi_{\parallel} = \beta S^2$, but at a certain temperature the susceptibility starts to deviate noticeably downward (it cannot catch up with $\frac{1}{3}\beta S(S+1)$). That temperature is of the order of D for $S = 1$ and $2D$ for $S = 3/2$ (figure 2), suggesting that the relevant/governing energy scale is again $T_1 = D(2S-1)$. Indeed, in units of DS^2 the extent of the bent range would be from $T = 0$ to $T_1/DS^2 \sim 2/S$ (see figure 5). This smoothly gives the connection with the classical result of full restoration of isotropy by letting $1/S \rightarrow 0$.

4.4.2. Approximate formula for $\bar{\chi}$. To confirm the previous estimates and scalings we have derived an approximate formula for $\bar{\chi}$ based on a few-levels treatment. It may also provide some insight into the origin of the deviations from $\chi_c = \frac{1}{3}\beta S(S+1)$.

We started looking at equation (2.26) for χ_{\perp} . One notices that letting $K_m \rightarrow 1$ (for instance, considering $K(\beta\Delta)$ plus $\Delta \sim 1/S$), the susceptibility is left as $\chi_{\perp}^{\text{iso}} = (\beta/2)\langle \ell_m^2 \rangle$, with $\langle \ell_m^2 \rangle := \sum_m \ell_m^2 e^{-\beta\varepsilon_m} / \mathcal{Z}_0$. Then, combining the average of the ladder factor $\ell_m^2 = S(S+1) - m(m+1)$ with the longitudinal susceptibility gives $\frac{1}{3}\chi_{\parallel} + \frac{2}{3}\chi_{\perp}^{\text{iso}} = \frac{1}{3}\beta S(S+1)$, explaining the notation $\chi_{\perp}^{\text{iso}}$. The actual susceptibility is obtained by adding and subtracting $\langle \ell_m^2 \rangle$ to equation (2.26):

$$\chi_{\perp} = \chi_{\perp}^{\text{iso}} + (\beta/2)\langle \ell_m^2 (K_m - 1) \rangle. \quad (4.6)$$

This form, times $2/3$ and combined with the longitudinal part (2.25), gives $\bar{\chi} = \chi_c + (\beta/3)\langle \ell_m^2 (K_m - 1) \rangle$. Thus in the second term (of transverse origin) we have isolated

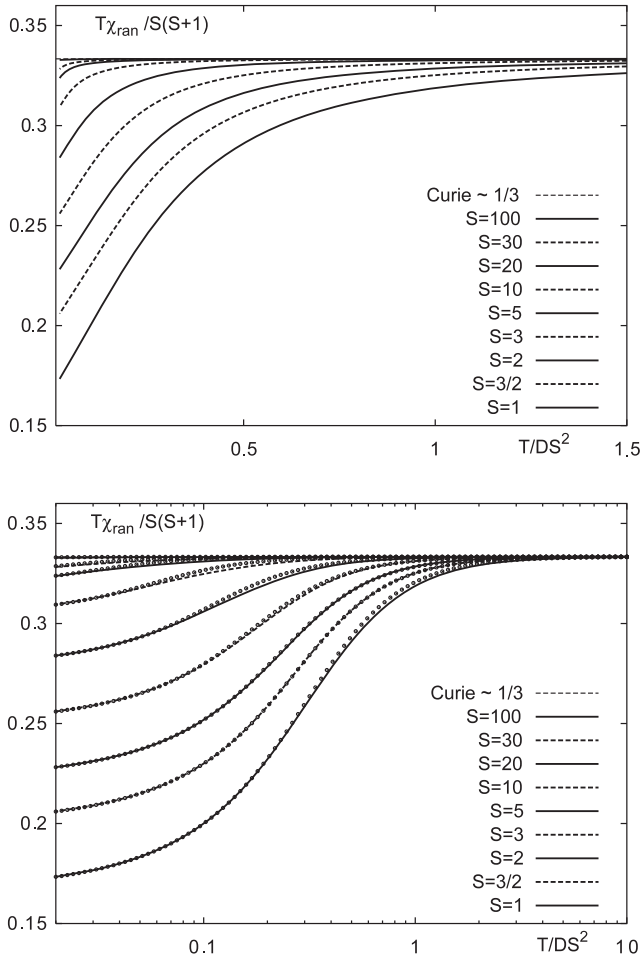


Figure 5. Random axes susceptibility versus temperature for various S , presented as $T\chi/S(S+1)$. (Notice the factor $1/2$ difference for $S=1$ with respect to figure 2, due to the normalization of χ .) The lower panel shows the same curves but over a wider temperature range in logarithmic scale, to test the approximate formula (4.7) (small circles).

the source of deviation from isotropy, but we have not done approximations yet²⁰.

To compute the suspect term $\langle \ell_m^2(K_m - 1) \rangle$ we just include the contribution of the two lowest levels (at each side; see table 3), getting the following susceptibility ($\Omega = \beta D(2S - 1)$):

$$\bar{\chi} \simeq \frac{1}{3} \underbrace{\beta S^2}_{\text{Curie}} + \frac{2}{3} \underbrace{\frac{1}{2D(1-1/2S)}}_{\text{restoring of Curie}} \frac{1 - e^{-\Omega}}{1 + e^{-\Omega}}. \quad (4.7)$$

From this expression we identify the Ising $\chi_{\parallel} \simeq \beta S^2$ at low temperatures. Besides, invoking $\Omega := \beta D(2S - 1) \gg 1$ at low T , one can read off the torque transverse susceptibility $\forall S$,

²⁰ By analogy with the classical superparamagnetic susceptibilities (4.5) one could introduce $\langle m^2 \rangle =: S(S+1)R'/R$ (which defines R'/R), and write ($\bar{T} = T/S(S+1)$)

$$\bar{T}\chi_{\parallel} = R'/R \quad \bar{T}\chi_{\perp} = (R - R')/2R + \text{corrections.}$$

The first term in χ_{\perp} corresponds to $\chi_{\perp}^{\text{iso}}$ (i.e. when combined with χ_{\parallel} and randomized gives Curie) and the corrections correspond to $\langle \ell_m^2(K_m - 1) \rangle$.

Table 3. Lowest energy levels for spin S at zero field $-\beta\varepsilon_m = d m^2$, ladder factors $\ell_m^2 = S(S+1) - m(m+1)$ and the transition frequencies $\beta\Delta_{mm+1} = \beta(\varepsilon_m - \varepsilon_{m+1}) = d(2m+1)$. The approximate partition function is $Z_0 \simeq 2(e^{-\beta\varepsilon_S} + e^{-\beta\varepsilon_{S-1}}) = 2e^{-\beta\varepsilon_S}(1 + e^{-\Omega})$ (cf [48, appendix A]).

m	$-\beta\varepsilon_m$	ℓ_m^2	$\beta\Delta_{mm+1}$
$-S$	dS^2	$2S$	$-d(2S-1) =: -\Omega$
$-S+1$	$d(S-1)^2$	—	—
$+S-1$	$d(S-1)^2$	$2S$	$+d(2S-1) =: +\Omega$
$+S$	dS^2	0	—

namely

$$\chi_{\perp}(T=0) = \frac{1}{2D(1-1/2S)}. \quad (4.8)$$

This gives the familiar values $\chi_{\perp} = 1/D$ for $S=1$ and $\chi_{\perp} = 3/4D$ for $S=3/2$.

Equation (4.7) is governed by the level difference $\Omega := \beta\Delta_{S,S-1}$, as expected from our lowest-level approximation. We have plotted it together with the exact $\bar{\chi}$ curves in the lower panel of figure 5. The description it provides is reasonably good at all temperatures, for all spin values, and quite good for $S=3/2$ and 2.

Multiplying now equation (4.7) by T and using $\beta D(1 - 1/2S) = \Omega/2S$ we can write the compact form

$$T\bar{\chi} \simeq \frac{S}{3} \left(S + \frac{2}{\Omega} \frac{1 - e^{-\Omega}}{1 + e^{-\Omega}} \right), \quad \Omega = \beta D(2S - 1). \quad (4.9)$$

This gives the S -dependent intercept of the χ axis at $T=0$ of figure 5 and the initial linear growth at low temperatures ($1/\Omega \propto T$ with $e^{-\Omega} \simeq 0$). But equation (4.9) happens to capture as well the restoring of Curie at high T ($\Omega \ll 1$). Indeed, Taylor-expanding $(2/\Omega)(1 - e^{-\Omega})/(1 + e^{-\Omega}) \simeq 1 - \Omega^2/12$, the constant term nicely produces $\frac{1}{3}S(S+1)$, the Curie constant. The second term can then be used to estimate the onset of deviations from χ_c . Fixing a 5% deviation, i.e. $\Omega^2/12 \simeq 0.05$, and writing $\Omega = (DS^2/T)(2S-1)/S^2$ yields $T/DS^2 \sim 5/2S$, in agreement with our previous estimate $2/S$.

As for the use of the approximate $\bar{\chi}$ one should bear in mind that equation (4.7) was derived under low T conditions (few populated levels). However, the reasonable agreement with the exact curves in the whole temperature range, and for all S , indicates that it could be used safely in modelization of uniaxial magnets with axes distributed at random.

5. Summary

The understanding of the properties of paramagnets belongs to a long tradition linking magnetism, quantum mechanics and statistical mechanics. Our aim here has been to extend the theoretical framework to permit the study of some equilibrium problems for arbitrary values of the spin. In this frame, one can connect from landmark results for quantum paramagnets (Curie–Brillouin, transverse response of anisotropic spins) all the way up to the theory of classical superparamagnets, developed for magnetic nanoparticles, and revived with the young molecular magnetic clusters (single-molecule magnets). We have used the language of magnetism throughout, but

the formalism is closely related to the effective big-spin description of collections of two-level systems used in atomic optics and two-mode Bose condensates [19–21].

We focused on uniaxial spins and the temperature dependence of the magnetic susceptibility, due to its traditional significance and its routine use as a characterization tool. We investigated three features: (1) the crossover of the longitudinal susceptibility from Curie to the two-state regime, induced by the magnetic anisotropy, (2) the peak in the transverse χ_{\perp} versus T and (3) deviations of the random ensemble susceptibility from the Curie law (absent in the classical limit). We identified and characterized the relevant energy/temperature parameters governing the phenomenology and studied how they scale with S . We did this starting from small spins $S = 1, 3/2, 2$, then moderate $S = 5, 10, \dots$ and eventually big spins $S = 30, 50, 100$, connecting with classical superparamagnetic phenomenology.

The equations we employed do not rely on Van Vleck's method, as they follow from the general Kubo correlator formalism of linear-response theory. We worked and particularized this formalism, with the above problems in mind, to produce ready-to-use formulae (equations (2.25) and (2.26)), which only require the input of the unperturbed spectrum and angular-momentum ladder factors.

We also derived approximate expressions and assessed their ranges of validity. This turned out to be quite good for the lowest-level approximation (4.7) to the susceptibility of the randomly oriented ensemble. It could be safely used as a compact modelization of susceptibility data for arbitrary S in such an experimentally relevant case. In real magnets, however, the unperturbed Hamiltonian will include terms non-diagonal in the standard basis, like DS_{\pm}^2 or KS_{\pm}^4 . These terms were not accounted for in the derivation of the approximate expression (4.7) and, when relevant, one should turn back to the more general equation (2.20).

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