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Thermodynamic perturbation theory for dipolar superparamagnets

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Thermodynamic perturbation theory is employed to derive analytical expressions for the equilibrium linear susceptibility and specific heat of lattices of anisotropic classical spins weakly coupled by the dipole-dipole interaction. The calculation is carried out to the second order in the coupling constant over the temperature, while the single-spin anisotropy is treated exactly. The temperature range of applicability of the results is, for weak anisotropy ($A/k_{\mathrm{B}}T \ll 1$), similar to that of ordinary high-temperature expansions, but for moderately and strongly anisotropic spins ($A/k_{\mathrm{B}}T \gtrsim 1$) it can extend down to the temperatures where the superparamagnetic blocking takes place ($A/k_{\mathrm{B}}T \sim 25$), provided only that the interaction strength is weak enough. Besides, taking exactly the anisotropy into account, the results describe as particular cases the effects of the interactions on isotropic ($A=0$) as well as strongly anisotropic ($|A| \to \infty$) systems (discrete orientation model and plane rotators).

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I. INTRODUCTION

In paramagnetic systems the relative weakness of the dipole-dipole interaction between magnetic ions results in characteristic temperatures lying in the range of 0.01–0.1 K. Besides, the dipolar coupling usually coexists with the exchange interaction. However, for superparamagnets (nanoscale solids or clusters whose net spin rotates thermally activated in the magnetic anisotropy potential), the exchange or other competing interactions can usually be discarded and the dipole-dipole interaction can be studied in pure form. In addition, the size of their typical magnetic moments ($S \sim 10^2$–10^5) shifts the relevant temperatures up to the range of a few K, facilitating greatly the experimental study of this interaction.[1]

The calculation of the relevant statistical-mechanical quantities constitutes a formidable problem in most many-body systems. Apart from various specific solution ansatzs, a number of systematic expansions (in the density, coupling parameter, etc.) have been developed for weak interactions.[2] In spin and dipole systems, the moment method of Van Vleck[3,4] (a high-temperature expansion of the partition function) permits us to study the equilibrium properties in the absence of cooperative phenomena. This technique is one of the few analytical tools available to handle systems coupled by the dipole-dipole interaction, due to the long-range and reduced symmetry of this interaction.

An important property of superparamagnets is their magnetic anisotropy, which results in a number of spin orientations of minimum energy separated by potential barriers. For uniaxial spins[5] the characteristic time for the thermoactivated rotation of the spin over the anisotropy barrier A can approximately be written as

$$\tau \simeq \tau_0 \exp(A/k_{\mathrm{B}}T), \tag{1.1}$$

where τ_0 is weakly temperature dependent and takes values $\tau_0 \sim 10^{-10}$–10^{-12} s for magnetic nanoparticles. Then, for a given measurement time t_{m} the system exhibits its thermal-equilibrium response when the *condition of superparamagnetism*, $t_{\mathrm{m}} \gg \tau$, is obeyed, which corresponds to the temperature range (in units of A/k_{B}):

$$\ln(t_{\mathrm{m}}/\tau_0) > A/k_{\mathrm{B}}T \geq 0. \tag{1.2}$$

In "static" measurements ($t_{\mathrm{m}} \sim 1$–100 s), due to the small value of τ_0, this equilibrium range extends down to very low temperatures ($25 > A/k_{\mathrm{B}}T$), showing that the naive ascription of superparamagnetism to the range in which "the thermal energy is comparable or larger than the anisotropy energy" ($1 \gtrsim A/k_{\mathrm{B}}T$) is unduly restrictive. Indeed, as T decreases the system displays different behaviors ranging from almost isotropic ($A/k_{\mathrm{B}}T \ll 1$), then moderately anisotropic ($A/k_{\mathrm{B}}T \sim 1$), and eventually strongly anisotropic ($A/k_{\mathrm{B}}T \gg 1$) *without leaving the equilibrium regime*. Therefore descriptions based on the assumption of isotropic behavior or the opposite discrete-orientation or plane-rotator approximations (for easy-axis and easy-plane anisotropy) necessarily have a reduced range of validity in superparamagnets.

Due to the mentioned characteristics of the dipole-dipole coupling and the difficulties introduced by the anisotropy, most rigorous calculations in interacting superparamagnets have been done by numerical simulation techniques.[6] In this paper we apply thermodynamic perturbation theory[7] to calculate analytically the linear susceptibility and the specific heat of lattices of uniaxial classical spins coupled by the dipole-dipole interaction, accounting exactly (nonperturbatively) for their anisotropy energy. Along with the study of the dependence on the shape of the system of certain quantities (due to the long range of the dipole-dipole interaction[8]), our treatment permits us to investigate the effects of the strength and sign of the anisotropy, as well as of the orientational distribution of anisotropy axes.

We find that for systems with axes *oriented at random* the corrections to the specific heat and the linear susceptibility become independent of the anisotropy (at least to second order in the interaction coupling) in certain spatial arrangements of the spins (e.g., cubic or completely disordered). The latter is a generalization to interacting systems of the well-known absence of anisotropy effects on the equilibrium linear susceptibility of dipoles with random anisotropy (discussed in Ref. 4). However, apart from the important exception of random axes, the anisotropy is an essential element in the determination of the corrections due to the interactions. This is illustrated with the response of systems with *parallel* anisotropy axes, where an ordinary high-temperature expansion, either disregarding the anisotropy or in the discrete orientation limit, poorly describes the susceptibility curves (computed for comparison by Monte Carlo simulation), while the thermodynamic perturbation theory describes the results with reasonable accuracy.

II. THERMODYNAMIC PERTURBATION THEORY FOR INTERACTING DIPOLES

In this section we introduce the spin system studied and discuss the application of perturbation theory to calculate approximately thermodynamic quantities.

A. Hamiltonian of a system of interacting anisotropic spins

Let us consider a system of N magnetoanisotropic spins coupled by the dipole-dipole interaction. The magnetic anisotropy energy is assumed to be uniaxial,

$$E_{\mathrm{a}}=-A\sum_i (\vec{s}_i\cdot\vec{n}_i)^2, \tag{2.1}$$

where A is the anisotropy parameter (for magnetic nanoparticles $A=KV$, where K and V are the anisotropy constant and volume), and $\vec{s}_i$ and $\vec{n}_i$ are, respectively, unit vectors along the magnetic moment and anisotropy axis of the ith spin. The dipole-dipole interaction energy can be written as

$$E_{\mathrm{d}}=-\frac{\mu_0 m^2}{4\pi a^3}\sum_{i>j}\omega_{ij}, \quad \omega_{ij}=\vec{s}_i\cdot\mathbf{G}_{ij}\cdot\vec{s}_j, \tag{2.2}$$

where m is the magnitude of the magnetic moment, a is an appropriate characteristic length (see below), and

$$\mathbf{G}_{ij}=\frac{1}{r_{ij}^3}(3\,\hat{r}_{ij}\hat{r}_{ij}-\mathbf{1}), \tag{2.3}$$

$$\vec{r}_{ij}=\vec{r}_i-\vec{r}_j, \quad \hat{r}_{ij}=\vec{r}_{ij}/r_{ij}. \tag{2.4}$$

Here $\mathbf{1}$ is the unit tensor and $\vec{r}_{ij}$ the vector joining the sites i and j (measured in units of a). The action of a tensor dyadic $\mathbf{T}=\vec{u}\,\vec{v}$ on a vector $\vec{w}$ is the usual one $(\vec{u}\,\vec{v})\vec{w}\equiv\vec{u}(\vec{v}\cdot\vec{w})$, and hence the tensor $\mathbf{G}_{ij}$, when multiplied with $\vec{s}_j$, gives (except for a constant) the field at the position of the ith dipole created by $\vec{s}_j$.

For notational simplicity we are assuming that the parameters characterizing the different dipoles are identical, but it is immediate to generalize the expressions for different anisotropy constants, magnetic moments, volumes, etc. Similarly, although the assumption of uniaxial anisotropy is not necessary until the end of the calculation we made it here for definiteness. Concerning the characteristic length a, it is defined in such a way that a^3 is the mean volume around each spin. Thus a is the lattice constant in a simple cubic arrangement, and for nanoparticles the volume concentration of particles is $c=V/a^3$.

Finally, introducing $\beta=1/k_{\mathrm{B}}T$ and the following dimensionless quantities (anisotropy and coupling constant relative to the thermal energy),

$$\sigma=\frac{A}{k_{\mathrm{B}}T}, \quad \xi_{\mathrm{d}}=\frac{\mu_0 m^2}{4\pi a^3}\frac{1}{k_{\mathrm{B}}T}, \tag{2.5}$$

we can write the total energy $E=E_{\mathrm{a}}+E_{\mathrm{d}}$ as

$$-\beta E=\sigma\sum_i (\vec{s}_i\cdot\vec{n}_i)^2+\xi_{\mathrm{d}}\sum_{i>j}\omega_{ij}. \tag{2.6}$$

Note that the interaction strength can also be measured by the temperature-independent coupling parameter

$$h_{\mathrm{d}}=\xi_{\mathrm{d}}/2\sigma, \tag{2.7}$$

which is the magnitude of the field (measured in units of the maximum anisotropy field $\mu_0 H_K=2A/m$) produced at a given position by a dipole at a distance a.[9]

B. Equilibrium linear susceptibility and specific heat

The thermal-equilibrium average of any quantity $B(\vec{s}_1,\ldots,\vec{s}_N)$ is given by

$$\langle B\rangle=\frac{1}{Z}\int d\Gamma\, B\exp(-\beta E), \tag{2.8}$$

where $Z=\int d\Gamma\exp(-\beta E)$ is the partition function. In classical spins the different states correspond to different spin orientations so that $d\Gamma=\Pi_i d\Omega_i$, with $d\Omega_i=d^2\vec{s}_i/2\pi$.

The linear susceptibility is defined as the derivative of the magnetization $(1/N)\langle\Sigma_i\vec{s}_i\rangle$ with respect to the *external* magnetic field (which is the experimentally manipulable quantity in contrast to the internal macroscopic field). However, from basic statistical mechanics we know that the response to a probing field $\Delta\vec{H}$ can be obtained in terms of suitable averages of the net spin taken in the absence of $\Delta\vec{H}$. If in addition there is no external *bias* field applied, the susceptibility is simply given by

$$\chi=\frac{\mu_0 m^2}{k_{\mathrm{B}}T}\frac{1}{N}\langle s_z^2\rangle, \quad s_z=\sum_i (\vec{s}_i\cdot\vec{h}), \tag{2.9}$$

where $\vec{h}$ is a unit vector along $\Delta\vec{H}$ and s_z is the field projection of the net moment. The specific heat at constant volume $c_v=\partial\langle E\rangle/\partial T$ can be obtained directly from Z as

$$\frac{c_v}{k_{\mathrm{B}}}=\beta^2\frac{\partial^2}{\partial\beta^2}(\ln Z)=\sigma^2\frac{\partial^2}{\partial\sigma^2}(\ln Z), \tag{2.10}$$

where to take the σ derivative, the coupling parameter ξ_{d} is expressed as $\xi_{\mathrm{d}}=2\sigma h_{\mathrm{d}}$ [Eq. (2.7)]. As in the calculation of χ, we only consider the zero-field specific heat.[10]

C. Thermodynamic perturbation theory

We shall now use thermodynamic perturbation theory,[7] to expand the Boltzmann distribution $W = Z^{-1}\exp(-\beta E)$ in powers of ξ_{d}. This will lead to an expression of the form

$$W = W_{\mathrm{a}}(1 + \xi_{\mathrm{d}} F_1 + \tfrac{1}{2}\xi_{\mathrm{d}}^2 F_2 + \cdots), \tag{2.11}$$

where F_1 is linear in E_{d} (and hence quadratic in the spins), F_2 is up to quadratic in E_{d} (quartic in the $\vec{s}_i$), and

$$W_{\mathrm{a}} = Z_{\mathrm{a}}^{-1}\exp(-\beta E_{\mathrm{a}}), \tag{2.12}$$

is the Boltzmann distribution of the noninteracting ensemble. Therefore the calculation of an observable $\langle B\rangle$ is reduced to the calculation of averages weighted by W_{a} (denoted $\langle\cdot\rangle_{\mathrm{a}}$) of typically low grade powers of the spin variables: $\langle B\rangle_{\mathrm{a}}$, $\langle BF_1\rangle_{\mathrm{a}}$, $\langle BF_2\rangle_{\mathrm{a}}$, etc. An ordinary high-temperature expansion corresponds to expand Eq. (2.12) further in powers of $\beta = 1/k_{\mathrm{B}}T$. In the present calculation, however, the averages are kept weighted over W_{a}, so they will be exact in the magnetic anisotropy and only perturbational in the dipolar interaction.[11]

A convenient way of performing the expansion in powers of ξ_{d} is to introduce the Mayer functions f_{ij} defined by $1 + f_{ij} = \exp(\xi_{\mathrm{d}}\omega_{ij})$, which permits us to write the exponential in the Boltzmann factor as

$$\exp(-\beta E) = \exp(-\beta E_{\mathrm{a}})\prod_{i>j}(1 + f_{ij}). \tag{2.13}$$

Expanding the product to second order in the f_{ij} gives

$$\prod_{i>j}(1 + f_{ij}) = 1 + \xi_{\mathrm{d}} G_1 + \tfrac{1}{2}\xi_{\mathrm{d}}^2 G_2 + O(\xi_{\mathrm{d}}^3), \tag{2.14}$$

where[12]

$$G_1 = \sum_{i>j}\omega_{ij}, \tag{2.15}$$

$$G_2 = \sum_{i>j}\omega_{ij}^2 + \sum_{i>j}\sum_{k>l}\omega_{ij}\omega_{kl}q_{ik:jl}q_{il:jk}, \tag{2.16}$$

and the symbol $q_{ik:jl}$ annihilates terms containing duplicate pairs: $q_{ik:jl} = \frac{1}{2}(2 - \delta_{ik} - \delta_{jl})(1 + \delta_{ik})(1 + \delta_{jl})$.

To obtain the average of any quantity B we introduce the expansion (2.14) in both the numerator and denominator of $\langle B\rangle = \int d\Gamma\, B\exp(-\beta E)/\int d\Gamma\exp(-\beta E)$, and work out the expansion of the quotient, getting[13]

$$\begin{aligned}\langle B\rangle \simeq \langle B\rangle_{\mathrm{a}} &+ \xi_{\mathrm{d}}[\langle B\,G_1\rangle_{\mathrm{a}} - \langle B\rangle_{\mathrm{a}}\langle G_1\rangle_{\mathrm{a}}] + \tfrac{1}{2}\xi_{\mathrm{d}}^2\{\langle B\,G_2\rangle_{\mathrm{a}} \\ &- \langle B\rangle_{\mathrm{a}}\langle G_2\rangle_{\mathrm{a}} - 2\langle G_1\rangle_{\mathrm{a}}[\langle B\,G_1\rangle_{\mathrm{a}} - \langle B\rangle_{\mathrm{a}}\langle G_1\rangle_{\mathrm{a}}]\}.\end{aligned}$$

However, since in our case $W_{\mathrm{a}}(-\vec{s}_i) = W_{\mathrm{a}}(\vec{s}_i)$ (because the single-spin anisotropy has inversion symmetry and there is no bias field) and in $G_1 = \Sigma_{i>j}\omega_{ij}$ a dipole does not interact with itself, the result $\langle G_1\rangle_{\mathrm{a}} = 0$ holds. Under these conditions we finally find the simpler form

$$\langle B\rangle \simeq \langle B\rangle_{\mathrm{a}} + \xi_{\mathrm{d}}\langle B\,G_1\rangle_{\mathrm{a}} + \tfrac{1}{2}\xi_{\mathrm{d}}^2[\langle B\,G_2\rangle_{\mathrm{a}} - \langle B\rangle_{\mathrm{a}}\langle G_2\rangle_{\mathrm{a}}]. \tag{2.17}$$

To complete the calculation we need to obtain averages of low grade powers of $\vec{s}$ weighted by the noninteracting distribution (moments), which is the only place where one needs to specify the form of E_{a}. We can write the susceptibility and specific heat to second order in ξ_{d} using up to fourth-order moments, which are calculated in Appendix A [Eqs. (A1) and (A2)] for the uniaxial distribution $W_{\mathrm{a}} \propto \exp[\sigma(\vec{s}\cdot\vec{n})^2]$. For instance, the first two moments read $\langle(\vec{c}_1\cdot\vec{s})\rangle_{\mathrm{a}} = 0$ and

$$\langle(\vec{c}_1\cdot\vec{s})(\vec{c}_2\cdot\vec{s})\rangle_{\mathrm{a}} = \frac{1 - S_2}{3}\vec{c}_1\cdot\vec{c}_2 + S_2(\vec{c}_1\cdot\vec{n})(\vec{c}_2\cdot\vec{n}),$$

where the $\vec{c}_n$ are arbitrary constant vectors and S_l is the average of the lth Legendre polynomial $P_l(z)$ over W_{a}:

$$S_l(\sigma) = \langle P_l(\vec{s}\cdot\vec{n})\rangle_{\mathrm{a}}. \tag{2.18}$$

In particular, $S_0 = 1$ and $S_2(\sigma) = \frac{1}{2}\langle 3(\vec{s}\cdot\vec{n})^2 - 1\rangle_{\mathrm{a}}$ can be expressed in terms of familiar special functions (error functions or the Dawson integral), while other S_l appearing in higher-order moments can be obtained by means of the recurrence relation they satisfy [Eq. (A8)].

III. ANALYTICAL EXPRESSIONS FOR THE SUSCEPTIBILITY AND SPECIFIC HEAT

We shall now present the general form of the perturbative expressions for the susceptibility and specific heat and discuss their properties in some important cases.

A. Linear susceptibility

Using the results of the previous section, we have averaged the square of the field projection of the net spin [$B = (\Sigma_i\vec{s}_i\cdot\vec{h})^2$], which yields an expansion for the equilibrium linear susceptibility [Eq. (2.9)] of the form

$$\chi = \frac{\mu_0 m^2}{k_{\mathrm{B}}T}(a_0 + \xi_{\mathrm{d}} a_1 + \tfrac{1}{2}\xi_{\mathrm{d}}^2 a_2). \tag{3.1}$$

The lengthy general expressions for the coefficients a_n, which include sums over the lattice of the dipolar tensor $\mathbf{G}_{ij}$ and the S_l, are written in full in Appendix B.

The coefficients a_n simplify notably for some orientational distributions of the anisotropy axes. For systems with parallel axes (e.g., single crystals of magnetic molecular clusters, or a ferrofluid frozen in a strong field), the coefficients for the longitudinal response read

$$a_{0,\parallel} = \frac{1 + 2S_2}{3}, \tag{3.2}$$

$$a_{1,\parallel} = \frac{1 + 4S_2 + 4S_2^2}{9}\mathcal{C}, \tag{3.3}$$

$$
\begin{aligned}
\tfrac{1}{2}a_{2,\parallel}= & -\frac{1+4S_2+4S_2^2}{27}[(1-S_2)(\overline{\mathcal{R}}-\mathcal{S})+3S_2(\mathcal{T}-\mathcal{U})] \\
& +\frac{7+10S_2-35S_2^2+18S_4}{315}[(1-S_2)\mathcal{V} \\
& +3S_2(\mathcal{T}-\tfrac{1}{3}\overline{\mathcal{R}})],
\end{aligned}
\tag{3.4}
$$

where $\mathcal{C}$, $\mathcal{R}$ ($\overline{\mathcal{R}}$), $\mathcal{S}$, $\mathcal{T}$, $\mathcal{U}$, and $\mathcal{V}$ are certain lattice sums whose properties are discussed below.

To obtain the susceptibility when the anisotropy axes are distributed at random, we average the general expressions for the a_n over $\vec{n}$, with help from Eqs. (A11) and (A12) (with $\vec{s}\to\vec{n}$), getting

$$a_{0,\mathrm{ran}}=\frac{1}{3}, \tag{3.5}$$

$$a_{1,\mathrm{ran}}=\frac{1}{9}\mathcal{C}, \tag{3.6}$$

$$\tfrac{1}{2}a_{2,\mathrm{ran}}=-\frac{1}{27}(\overline{\mathcal{R}}-\mathcal{S})+\frac{1}{45}(1-S_2^2)\mathcal{V}. \tag{3.7}$$

Note that in the limit of isotropic spins (where $S_l\to 0$) the results for coherent axes and for random anisotropy duly coincide.

B. Specific heat

To obtain the specific heat we can expand directly the partition function in powers of ξ_{d} by introducing the expanded Boltzmann factor [Eqs. (2.13) and (2.14)] in the definition of Z,

$$
\begin{aligned}
Z= & \int d\Gamma\,\exp(-\beta E_a)(1+\xi_{\mathrm{d}}G_1+\tfrac{1}{2}\xi_{\mathrm{d}}^2G_2) \\
= & Z_{\mathrm{a}}(1+\tfrac{1}{2}\xi_{\mathrm{d}}^2\langle G_2\rangle_{\mathrm{a}}),
\end{aligned}
\tag{3.8}
$$

where the linear term vanishes because $\langle G_1\rangle_{\mathrm{a}}=0$. Then c_v is obtained [Eq. (2.10)] by differentiating the logarithm of the above expansion, which poses no problem of the type of expanding a quotient, since to second order in ξ_{d} we can use $\ln(1+x\xi_{\mathrm{d}}^2)\simeq x\xi_{\mathrm{d}}^2$. The result has the form

$$\frac{c_v}{Nk_{\mathrm{B}}}=\sigma^2 b_0+\tfrac{1}{2}\xi_{\mathrm{d}}^2 b_2, \tag{3.9}$$

where the zeroth-order coefficient

$$b_0=\frac{4}{315}(18S_4-35S_2^2+10S_2+7), \tag{3.10}$$

gives the specific heat in the absence of interactions.

The general formula for b_2 is given in Appendix C [Eq. (C1)]. Again, it simplifies for coherent axes and for random anisotropy. In the first case ($\vec{n}_i=\vec{n},\forall i$) we obtain

$$
\begin{aligned}
b_{2,\parallel}= & \tfrac{1}{3}\{1-S_2^2-4\sigma S_2S_2'-\sigma^2[S_2S_2''+(S_2')^2]\}\mathcal{R} \\
& +\tfrac{1}{3}(2S_2(1-S_2)+4\sigma S_2'(1-2S_2) \\
& +\sigma^2\{S_2''-2[S_2S_2''+(S_2')^2]\})\mathcal{V}+\{S_2^2+4\sigma S_2S_2' \\
& +\sigma^2[S_2S_2''+(S_2')^2]\}\mathcal{T},
\end{aligned}
\tag{3.11}
$$

where $f'=df/d\sigma$. For randomly distributed axes, on averaging the general expression for b_2 over $\vec{n}$ by means of Eq. (A13), one gets

$$b_{2,\mathrm{ran}}=\tfrac{1}{3}\mathcal{R}. \tag{3.12}$$

This is the same correction term as that obtained for *isotropic* spins by Waller[14] and Van Vleck.[3]

C. Lattice sums

An essential element of the expressions derived for χ and c_v are the following "lattice sums"

$$\mathcal{C}=\frac{1}{N}\sum_i\sum_{j\neq i}\vec{h}\cdot\mathbf{G}_{ij}\cdot\vec{h}, \tag{3.13}$$

$$\mathcal{R}=\frac{2}{N}\sum_i\sum_{j\neq i}r_{ij}^{-6}, \tag{3.14}$$

$$\overline{\mathcal{R}}=\frac{1}{N}\sum_i\sum_{j\neq i}\vec{h}\cdot\mathbf{G}_{ij}\cdot\mathbf{G}_{ij}\cdot\vec{h}, \tag{3.15}$$

$$\mathcal{S}=\frac{1}{N}\sum_i\sum_{j\neq i}\sum_{k\neq j}\vec{h}\cdot\mathbf{G}_{ij}\cdot\mathbf{G}_{jk}\cdot\vec{h}, \tag{3.16}$$

$$\mathcal{T}=\frac{1}{N}\sum_i\sum_{j\neq i}(\vec{h}\cdot\mathbf{G}_{ij}\cdot\vec{h})^2, \tag{3.17}$$

$$\mathcal{U}=\frac{1}{N}\sum_i\sum_{j\neq i}\sum_{k\neq j}(\vec{h}\cdot\mathbf{G}_{ij}\cdot\vec{h})(\vec{h}\cdot\mathbf{G}_{jk}\cdot\vec{h}), \tag{3.18}$$

$$\mathcal{V}=\frac{1}{N}\sum_i\sum_{j\neq i}r_{ij}^{-3}\vec{h}\cdot\mathbf{G}_{ij}\cdot\vec{h} \tag{3.19}$$

(replace $\vec{h}$ by $\vec{n}$ in the formulas for c_v). Considering the structure of these sums along with the form of the dipolar tensor $\mathbf{G}_{ij}$ [Eq. (2.2)], some physical interpretation can be provided for the different terms in the perturbative series.[12] The first-order term a_1 incorporates through $\mathcal{C}$ the *direct* action ($j\to i$) on each spin of the remainder spins, when aligned along the probing field. No term of this type appears in the specific heat since the absence of any external field yields $b_1\equiv 0$. The second-order terms a_2 and b_2 involve lattice sums including products of $\mathbf{G}_{ij}$ with $\mathbf{G}_{jk}$ so they take into account the action on a given spin of the others but through intermediate spins (*indirect* action $k\to j\to i$). In particular, if $k=i$ we have the *reaction* on the ith spin of its direct action on the remainder spins.

In the next section we shall compute χ and c_v for "sufficiently isotropic" lattices, in the sense of fulfilling $\Sigma(r_x)^n=\Sigma(r_y)^n=\Sigma(r_z)^n$, e.g., cubic and completely disordered lattices (incidentally, the type of arrangements for which in the classical Lorentz cavity-field calculation the contribution of the dipoles inside the ''small sphere'' vanishes). In these lattices we have two important results: (i) $\overline{\mathcal{R}}$ coincides with the more familiar lattice sum $\mathcal{R}$ (which justifies the notation) and (ii) $\mathcal{V}=0$.

D. Ordinary high-temperature expansions and other approximations

The effects of the anisotropy are included *exactly* in our formulas through the anisotropy-weighted averages of the Legendre polynomials $S_2(\sigma)$ and $S_4(\sigma)$, which modulate the different contributions and introduce an extra dependence on the temperature via $\sigma=A/k_\mathrm{B}T$. This reflects the fact that the dipolar field at a given site is different if the source spins are almost freely rotating (high T, $S_l\to 0$) or, for example, lay almost parallel to their respective anisotropy axes (low T, $S_l\to 1$).

The approximate behavior of S_2 and S_4 for weak ($|\sigma|\ll 1$) and strong ($|\sigma|\gg 1$) anisotropy is[15]

$$S_2(\sigma)=\begin{cases} \dfrac{2}{15}\sigma+\dfrac{4}{315}\sigma^2+\cdots & |\sigma|\ll 1\\[2ex] 1-\dfrac{3}{2\sigma}-\dfrac{3}{4\sigma^2}+\cdots & \sigma\gg 1\\[2ex] -\dfrac{1}{2}\left(1+\dfrac{3}{2\sigma}\right)+\cdots & \sigma\ll -1,\end{cases} \tag{3.20}$$

$$S_4(\sigma)=\begin{cases} \dfrac{4}{315}\sigma^2+\cdots & |\sigma|\ll 1\\[2ex] 1-\dfrac{5}{\sigma}+\dfrac{25}{4\sigma^2}+\cdots & \sigma\gg 1\\[2ex] \dfrac{3}{8}\left(1+\dfrac{5}{\sigma}+\dfrac{35}{4\sigma^2}\right)+\cdots & \sigma\ll -1.\end{cases} \tag{3.21}$$

The results of an ordinary high-temperature expansion, in which all terms in $\exp(-\beta E)$ are expanded, correspond to replace S_2 and S_4 in the coefficients a_n and b_n by their weak anisotropy approximations. Besides, taking the $\sigma\to 0$ limit (where $S_l=0$) we get the known results for isotropic spins (in a slightly more general form, since the terms including $\mathcal{V}$ are usually omitted due to the lattices assumed[12,16]). In addition, substituting the above strong anisotropy formulas in χ and c_v we get these quantities in the discrete-orientation and plane-rotator cases (with the corresponding corrections in powers of $1/\sigma$).

IV. BEHAVIOR OF THE SUSCEPTIBILITY AND THE SPECIFIC HEAT

In this section we study the features of the susceptibility and specific heat emerging from the analytical expressions derived. We shall discuss the shape dependence of these quantities, investigate the dependence on the anisotropy (on both its strength and the axes distribution), and finally estimate the limits of validity of the expansions. For concreteness, we shall consider the behavior of spins with easy-axis anisotropy ($A>0$) in simple cubic lattices.

A. Shape dependence

Here we restrict our attention to systems with ellipsoidal shape, which is the geometry usually consider in studies of the dipole-dipole interaction because: (i) in the continuous limit the demagnetizing field is spatially homogeneous and parallel to the external field when this is along one of the three principal axes[17] and (ii) it covers as limit cases important geometries such as those of disks or long cylinders.

The long range of the dipole-dipole interaction leads to a shape dependence of the physical quantities in an external field[8] and hence of the linear susceptibility (which is a field derivative). In the expressions obtained, this shape dependence is borne by the slowly convergent lattice sums $\mathcal{C}$, $\mathcal{S}$, and $\mathcal{U}$. For the class of sufficiently isotropic lattices mentioned, these sums vanish in macroscopically large *spherical* systems, being nonzero otherwise. The sums $\mathcal{R}$ ($\overline{\mathcal{R}}$), $\mathcal{T}$, and $\mathcal{V}$, on the other hand, contain r_{ij}^{-6} (instead of r_{ij}^{-3} or $r_{ij}^{-3}r_{jk}^{-3}$), which makes them rapidly convergent and shape independent.[18]

Figure 1 shows the thermodynamic perturbation-theory susceptibility (thin lines) for $h_\mathrm{d}=\xi_\mathrm{d}/2\sigma=0.02$ and χ in the noninteracting limit (thick lines) for a system with parallel axes with the form of a prolate ellipsoid, a sphere, and an oblate ellipsoid (the symbols correspond to Monte Carlo simulations to be discussed below). For the nonspherical systems $\mathcal{C}\neq 0$,[19] and the corrections to the susceptibility are largely dominated by the first-order term, which corresponds to the direct action discussed above. The shape dependence is easily understood by recalling the behavior of two dipoles: if their axes are aligned, they minimize their dipole-dipole energy lying parallel along the line joining them, while if this line is perpendicular to the axes, they minimize the interaction energy pointing along opposite directions. Therefore in elongated systems the aligning effect dominates and χ is larger than the noninteracting susceptibility [Fig. 1(a)], while in oblate systems the opposite occurs with the associated decrease of χ [Fig. 1(c)]. In the sphere the direct term exactly cancels ($\mathcal{C}=0$), and negative second-order corrections (which incorporate indirect and reaction terms) determine the susceptibility [Fig. 1(b)].

Concerning the specific heat, due to the presence of the rapidly convergent lattice sums $\mathcal{R}$, $\mathcal{T}$, and $\mathcal{V}$, this quantity does not depend on the shape of the system. Physically, this is a consequence of the absence of linear term in Eq. (3.8), which follows from $\langle G_1\rangle_\mathrm{a}=0$, which in turn requires the absence of a bias field.

B. Anisotropy dependence

To illustrate the importance of taking the anisotropy into account, we are going to compare the thermodynamic perturbation-theory results with: (i) those obtained by an ordinary high-temperature expansion for zero anisotropy (the $S_l\to 0$ limit of our expressions) and (ii) the results in the discrete orientation limit ($S_l\to 1$).

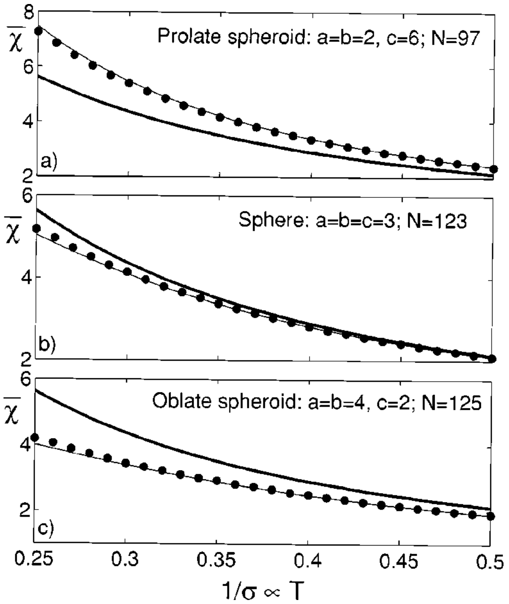

FIG. 1. Equilibrium linear susceptibility vs temperature for three different ellipsoidal systems with equation $x^2/a^2+y^2/b^2+z^2/c^2 \leq 1$ resulting in a system of N dipoles. The susceptibility is given in reduced units $\bar{\chi}=\chi(H_K/m)$, the spatial arrangement of the spins is simple cubic, and the probing field is applied along the anisotropy axes, which are *parallel* to the z axis. The thick lines are the equilibrium susceptibility of the corresponding noninteracting systems (they are equal in all three cases); thin lines are the susceptibilities including the corrections due to the dipolar interactions obtained by thermodynamic perturbation theory [Eq. (3.1)]; and the symbols represent the susceptibility obtained with a Monte Carlo method. The dipolar interaction strength is $h_d=\xi_d/2\sigma=0.02$. (For the prolate and oblate ellipsoids the second-order correction is very small in the temperature interval displayed and omitting it the curves visually coincide.)

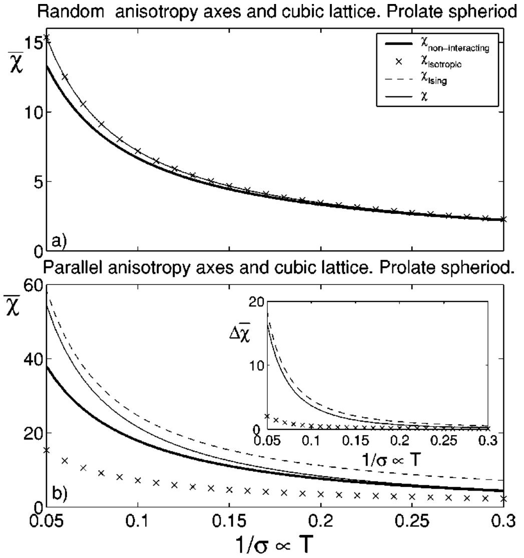

FIG. 2. Equilibrium linear susceptibility vs temperature for the same prolate ellipsoid as in Fig. 1(a) and the dipolar interaction strength $h_d=\xi_d/2\sigma=0.004$. The spins are arranged on a simple cubic lattice with (a) randomly distributed anisotropy axes and (b) parallel anisotropy axes. Thick lines are the susceptibilities for independent spins and thin lines are the susceptibilities obtained by thermodynamic perturbation theory. For comparison we have displayed χ obtained by a classical high-temperature expansion for isotropic spins (crosses) and for Ising spins (dashed line). Inset: Comparison of the corrections to the susceptibility due to interactions ($\Delta\chi=\chi-\chi_{\text{non-int}}$). (Note that the temperatures displayed are above the lower validity limit $\xi_d\sim 1/6$ estimated in the text: $1/\sigma=2h_d/\xi_d\sim 0.048$.)

In the cases of cubic or completely disordered lattices we already know that the lattice sum $\mathcal{V}$ vanishes. Then, the first corrections to the susceptibility due to the interactions become *exactly* independent of the anisotropy *if* the axes are distributed at random [see Eqs. (3.5)–(3.7) where the only anisotropy dependent term is multiplied by $\mathcal{V}$]. Therefore the susceptibility coincides with that obtained by an ordinary high-temperature expansion for isotropic dipoles (see Ref. 12; $\mathcal{V}=0$ was implicitly used in that work) but also with the perturbative χ for Ising-like spins with randomly distributed "Ising" axes [Fig. 2(a)]. This generalizes to interacting spins the well-known result, discussed in Ref. 4 (see also Ref. 20), i.e., the absence of anisotropy effects on the equilibrium linear susceptibility of systems with random anisotropy.

Nevertheless, when $\mathcal{V}\neq 0$ (as occurs in tetragonal lattices) the susceptibility will show some anisotropy dependence for random axes (although weak, since $\mathcal{V}\neq 0$ is accompanied by $\mathcal{C}\neq 0$ and χ is then dominated by the anisotropy independent first-order term). In any case, on inspecting Eqs. (3.2)–(3.4) one would expect important differences for parallel axes between the thermodynamic perturbation-theory results and those where the anisotropy is not included ($S_l\to 0$). This is what actually occurs, as Fig. 2(b) illustrates: the susceptibility is not only larger for parallel axes than for isotropic dipoles, but also the temperature dependence is stronger, owing to the extra, anisotropy-induced, temperature dependence of the coefficients a_n via $S_l(\sigma)$. This is clearly seen when comparing the correction terms $\Delta\chi$ themselves [inset of Fig. 2(b)].

Note that the susceptibilities in the isotropic and Ising cases constitute lower and upper bounds to the actual χ. The upper bound is slowly approached at low enough temperatures ($\sigma \gg 1$), completing in this way the crossover from isotropic behavior at high T to the discrete-orientation behavior at low T. Note finally that the lowest temperatures displayed ($\sigma\sim 20$) are still inside the range where an ordinary magnetization experiment yields the equilibrium response ($\sigma\sim 25$).

Concerning the specific heat, the part corresponding to the noninteracting system, b_0, does not depend on the anisotropy axes orientations. The reason is that if the spins are independent, they cannot probe the relative orientations of their axes and there is no preferential direction to compare their orientations with (as that of the probing field in the susceptibility). Thus the noninteracting specific heat (inset in Fig. 3) only reflects the individual behavior of the spins in their single-spin anisotropy potentials, and its peak (at $\sigma\sim 5$) reflects the "transition" from the isotropic behavior at high T (with $c_v \propto 1/T^2$) to the discrete orientation behavior at low T. This can

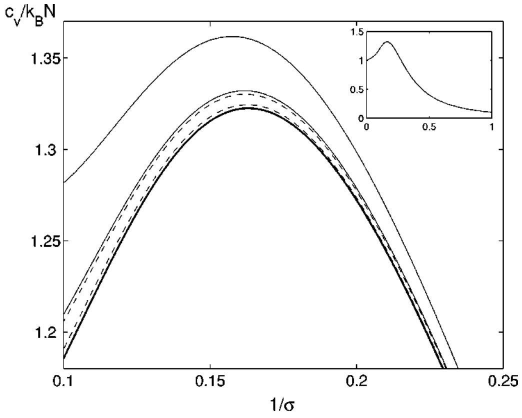

FIG. 3. Specific heat per spin vs temperature for noninteracting spins (thick line), and weakly interacting spins with randomly distributed anisotropy axes (dashed lines) and parallel axes (thin lines) arranged on a simple cubic lattice. In each case, $h_{\mathrm{d}}=\xi_{\mathrm{d}}/2\sigma=0.003$ and 0.006 from bottom to top. The inset shows the specific heat for noninteracting spins over a wider temperature interval.

be considered as a sort of Schottky peak, due in this case to the "depopulation" of the high-energy "barrier levels."[21]

The corrections due to the coupling depend naturally on the orientations of the axes. For a given axes distribution the specific heat increases with the interaction strength (Fig. 3), since an amount of heat injected in the system can partially be stored in the form of the potential energy of interaction. For the same reason, since the average of the interaction energy is larger (in magnitude) in systems with aligned axes, one would expect a larger c_v in this case. Figure 3 shows that the effect of the interaction is indeed stronger in a system with aligned axes than in a system with random anisotropy.

C. Validity limits of the perturbational results

Since the analytic expressions derived for χ and c_v are expansions valid in principle for $\xi_{\mathrm{d}}\ll 1$, which corresponds to $T\propto 1/\sigma\gg 2h_{\mathrm{d}}$ [Eq. (2.7)], the results will deviate appreciably from the exact quantities at sufficiently low T. In order to estimate the limits of validity, it would be desirable to compare the formulas with the results of some method treating the interactions without approximations. Besides, as the fundamentals of the expansion are the same for the different quantities, it would suffice to estimate the range of validity for one of them.

We have compared the analytical χ with the susceptibility computed by a Monte Carlo method (described in Appendix D), which except for statistical and finite sampling errors is exact to compute equilibrium properties. Returning to Fig. 1 we observe that χ obtained by thermodynamic perturbation theory (thin lines) describes accurately the simulated susceptibility (symbols) at high and intermediate T, while the results start to deviate slightly at the lowest temperatures displayed ($\sigma\sim 4$). Therefore, since $h_{\mathrm{d}}=0.02$ was used in this graph, an estimate of the lower temperatures attainable is $\xi_{\mathrm{d}}\sim 1/6$, which is milder than the *a priori* restriction $\xi_{\mathrm{d}}\ll 1$.

V. SUMMARY AND CONCLUSIONS

We have obtained approximate analytical expressions for the equilibrium linear susceptibility and specific heat of classical spins interacting via dipole-dipole interactions by means of thermodynamic perturbation theory. The formulas account for the interactions to second order in the coupling constant over temperature but are exact in the anisotropy. As the results are valid for any strength and sign of the anisotropy, provided only the interaction strength is weak enough ($\xi_{\mathrm{d}}\lesssim 1/6$), they include as particular cases the linear response and specific heat of isotropic as well as strongly anisotropic spins (discrete-orientation model and plane rotators).

The expressions derived also account for the different orientational distributions of anisotropy axes. For randomly distributed axes and sufficiently isotropic lattices (e.g., cubic or completely disordered), the linear susceptibility becomes independent of the anisotropy, at least to second order in the coupling constant. This extends to interacting systems the well-known absence of anisotropy effects on the equilibrium linear response of systems with random anisotropy. The same holds for the corrections to the specific heat due to the interactions (indeed, without restrictions on the lattice type). For a general axes distribution, however, the anisotropy effects do not disappear. The importance of including them has been illustrated in the case of coherent axes by showing the failure of ordinary high-temperature expansions (for either isotropic or strongly anisotropic spins) to describe the exact susceptibility in cases where the thermodynamic perturbation theory yields accurate results.

ACKNOWLEDGMENTS

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APPENDIX A: AVERAGES WEIGHTED WITH THE UNIAXIAL ANISOTROPY BOLTZMANN FACTOR

The averages we need to calculate are all of products of the form $I_m=\langle\prod_{n=1}^{m}(\vec{c}_n\cdot\vec{s})\rangle_{\mathrm{a}}$, where the $\vec{c}_n$ are arbitrary constant vectors. Introducing the polar and azimuthal angles of the spin, (ϑ,φ), we can write I_m as

$$I_m=\frac{\int_0^{2\pi}d\varphi\int_0^{\pi}d\vartheta\,\sin\vartheta\prod_{n=1}^{m}(\vec{c}_n\cdot\vec{s})\exp[\sigma(\vec{s}\cdot\vec{n})^2]}{\int_0^{2\pi}d\varphi\int_0^{\pi}d\vartheta\,\sin\vartheta\,\exp[\sigma(\vec{s}\cdot\vec{n})^2]}.$$

For odd m, I_m is an integral of an odd function over a symmetric interval and hence $I_m=0$. To calculate the susceptibility and specific heat to second order in ξ_{d}, we require I_2 and I_4, which will be calculated using symmetry arguments similar to those employed to derive the $\sigma=0$ unweighted averages (see, for instance, Ref. 22).

Note that I_2 is a scalar bilinear in $\vec{c}_1$ and $\vec{c}_2$. The most general scalar with this property that can be constructed with the vectors of the problem ($\vec{c}_1$, $\vec{c}_2$, and $\vec{n}$) has the form

$$I_2=A\vec{c}_1\cdot\vec{c}_2+B(\vec{c}_1\cdot\vec{n})(\vec{c}_2\cdot\vec{n}).$$

To find the coefficients A and B one chooses particular values for the $\vec{c}_n$: (i) If $\vec{c}_1 \| \vec{c}_2 \perp \vec{n}$ then $I_2 = A$. Thus, setting $\vec{n} = \hat{z}$ and $\vec{c}_1 = \vec{c}_2 = \hat{x}$, one has $\vec{s} \cdot \vec{n} = \cos\vartheta \equiv z$ and $(\vec{c}_1 \cdot \vec{s})(\vec{c}_2 \cdot \vec{s}) = (1 - z^2)\cos^2\varphi$, so the integral reads

$$A = \frac{\int_0^{2\pi} d\varphi \cos^2\varphi \int_{-1}^{1} dz (1 - z^2) \exp(\sigma z^2)}{\int_0^{2\pi} d\varphi \int_{-1}^{1} dz \exp(\sigma z^2)}$$

$$= \tfrac{1}{2}[1 - \langle z^2 \rangle_{\mathrm{a}}] = \frac{1 - S_2}{3},$$

where $S_2(\sigma) = \langle P_2(z) \rangle_{\mathrm{a}}$ is the average of the second Legendre polynomial $P_2(z) = \frac{1}{2}(3z^2 - 1)$ over the noninteracting distribution. (ii) If $\vec{c}_1 \| \vec{c}_2 \| \vec{n}$, then $I_2 = A + B$. Putting $\vec{n} = \vec{c}_1 = \vec{c}_2 = \hat{z}$ the integral is given by

$$A + B = \frac{\int_{-1}^{1} dz\, z^2 \exp(\sigma z^2)}{\int_{-1}^{1} dz \exp(\sigma z^2)} = \langle z^2 \rangle_{\mathrm{a}} = \frac{1 + 2S_2}{3}.$$

Therefore, since $I_2 = \langle (\vec{c}_1 \cdot \vec{s})(\vec{c}_2 \cdot \vec{s}) \rangle_{\mathrm{a}}$, we get for the second-order moment

$$\langle (\vec{c}_1 \cdot \vec{s})(\vec{c}_2 \cdot \vec{s}) \rangle_{\mathrm{a}} = \frac{1 - S_2}{3} \vec{c}_1 \cdot \vec{c}_2 + S_2 (\vec{c}_1 \cdot \vec{n})(\vec{c}_2 \cdot \vec{n}). \tag{A1}$$

We can similarly calculate I_4 by constructing the most general scalar fulfilling certain properties, getting

$$\begin{aligned}\langle (\vec{c}_1 \cdot \vec{s})(\vec{c}_2 \cdot \vec{s})(\vec{c}_3 \cdot \vec{s})(\vec{c}_4 \cdot \vec{s}) \rangle_{\mathrm{a}} = {} & \Delta_4[(\vec{c}_1 \cdot \vec{c}_2)(\vec{c}_3 \cdot \vec{c}_4) + (\vec{c}_1 \cdot \vec{c}_3)(\vec{c}_2 \cdot \vec{c}_4) + (\vec{c}_1 \cdot \vec{c}_4)(\vec{c}_2 \cdot \vec{c}_3)] + \Delta_2[(\vec{c}_1 \cdot \vec{c}_2)(\vec{c}_3 \cdot \vec{n})(\vec{c}_4 \cdot \vec{n}) \\ & + (\vec{c}_1 \cdot \vec{c}_3)(\vec{c}_2 \cdot \vec{n})(\vec{c}_4 \cdot \vec{n}) + (\vec{c}_1 \cdot \vec{c}_4)(\vec{c}_2 \cdot \vec{n})(\vec{c}_3 \cdot \vec{n}) + (\vec{c}_2 \cdot \vec{c}_3)(\vec{c}_1 \cdot \vec{n})(\vec{c}_4 \cdot \vec{n}) + (\vec{c}_2 \cdot \vec{c}_4)(\vec{c}_1 \cdot \vec{n}) \\ & \times (\vec{c}_3 \cdot \vec{n}) + (\vec{c}_3 \cdot \vec{c}_4)(\vec{c}_1 \cdot \vec{n})(\vec{c}_2 \cdot \vec{n})] + S_4 (\vec{c}_1 \cdot \vec{n})(\vec{c}_2 \cdot \vec{n})(\vec{c}_3 \cdot \vec{n})(\vec{c}_4 \cdot \vec{n}),\end{aligned} \tag{A2}$$

where Δ_2 and Δ_4 are combinations of the first $S_l(\sigma)$

$$\Delta_2 = \frac{1}{7}(S_2 - S_4), \quad \Delta_4 = \frac{S_4}{35} - \frac{2S_2}{21} + \frac{1}{15}. \tag{A3}$$

Therefore Eq. (A2) involves S_2 as well as $S_4(\sigma) = \langle P_4(z) \rangle_{\mathrm{a}}$, the average of the fourth Legendre polynomial $P_4(z) = \frac{1}{8}(35z^4 - 30z^2 + 3)$ with respect to W_{a}.

Finally, introducing the following tensor and scalar shorthands

$$\mathbf{\Gamma} = \frac{1 - S_2}{3}\mathbf{1} + S_2 \vec{n}\vec{n}, \tag{A4}$$

$$\mathbf{\Lambda} = \sqrt{\Delta_4}\mathbf{1} + \frac{\Delta_2}{\sqrt{\Delta_4}} \vec{n}\vec{n}, \quad \Omega = S_4 - 3\frac{\Delta_2^2}{\Delta_4}, \tag{A5}$$

where $\mathbf{1}$ is the identity tensor, the results for the moments can compactly be written as

$$\langle (\vec{c}_1 \cdot \vec{s})(\vec{c}_2 \cdot \vec{s}) \rangle_{\mathrm{a}} = (\vec{c}_1 \cdot \mathbf{\Gamma} \cdot \vec{c}_2), \tag{A6}$$

$$\begin{aligned}&\langle (\vec{c}_1 \cdot \vec{s})(\vec{c}_2 \cdot \vec{s})(\vec{c}_3 \cdot \vec{s})(\vec{c}_4 \cdot \vec{s}) \rangle_{\mathrm{a}} \\ &\quad = (\vec{c}_1 \cdot \mathbf{\Lambda} \cdot \vec{c}_2)(\vec{c}_3 \cdot \mathbf{\Lambda} \cdot \vec{c}_4) + (\vec{c}_1 \cdot \mathbf{\Lambda} \cdot \vec{c}_3)(\vec{c}_2 \cdot \mathbf{\Lambda} \cdot \vec{c}_4) \\ &\qquad + (\vec{c}_1 \cdot \mathbf{\Lambda} \cdot \vec{c}_4)(\vec{c}_2 \cdot \mathbf{\Lambda} \cdot \vec{c}_3) \\ &\quad + \Omega (\vec{c}_1 \cdot \vec{n})(\vec{c}_2 \cdot \vec{n})(\vec{c}_3 \cdot \vec{n})(\vec{c}_4 \cdot \vec{n}),\end{aligned} \tag{A7}$$

which facilitates the manipulation of the observables.

The quantities S_l can be computed using the following homogeneous three-term recurrence relation:[25]

$$\left[1 - \frac{2\sigma}{(2l-1)(2l+3)}\right] S_l - \frac{2\sigma}{2l+1}\left[\frac{l-1}{2l-1} S_{l-2} - \frac{l+2}{2l+3} S_{l+2}\right] = 0, \tag{A8}$$

knowing the first two terms: $S_0 = 1$ and S_2, which is given by

$$S_2 = \frac{3}{2}\left(\frac{e^{\sigma}}{\sigma Z_{\mathrm{a}}} - \frac{1}{2\sigma}\right) - \frac{1}{2}. \tag{A9}$$

The one-spin partition function $Z_{\mathrm{a}} = \int_{-1}^{1} dz \exp(\sigma z^2)$ can be written in terms of *error* functions of real and "imaginary" argument as

$$Z_{\mathrm{a}} = \begin{cases} \sqrt{\pi/\sigma}\, \mathrm{erfi}(\sqrt{\sigma}), & \sigma > 0 \\ \sqrt{\pi/|\sigma|}\, \mathrm{erf}(\sqrt{|\sigma|}), & \sigma < 0. \end{cases} \tag{A10}$$

The less familiar erfi(x) is related with the Dawson integral $D(x)$, so in the easy-axis case one can write $Z_{\mathrm{a}} = (2e^{\sigma}/\sqrt{\sigma}) D(\sqrt{\sigma})$ and compute $D(x)$ with the subroutine DAWSON of Ref. 23.

Note finally that in the isotropic limit ($S_l \to 0$), Eqs. (A1) and (A2) reduce to the known moments for the isotropic distribution,[12,22]

$$\langle (\vec{c}_1 \cdot \vec{s})(\vec{c}_2 \cdot \vec{s}) \rangle_{\mathrm{iso}} = \tfrac{1}{3} \vec{c}_1 \cdot \vec{c}_2, \tag{A11}$$

$$\langle(\vec{c}_1\cdot\vec{s})(\vec{c}_2\cdot\vec{s})(\vec{c}_3\cdot\vec{s})(\vec{c}_4\cdot\vec{s})\rangle_{\rm iso}$$
$$=\tfrac{1}{15}[(\vec{c}_1\cdot\vec{c}_2)(\vec{c}_3\cdot\vec{c}_4)+(\vec{c}_1\cdot\vec{c}_3)(\vec{c}_2\cdot\vec{c}_4)+(\vec{c}_1\cdot\vec{c}_4)(\vec{c}_2\cdot\vec{c}_3)]. \tag{A12}$$

These expressions are formally identical to those for the average of a quantity involving the anisotropy axes $\vec{n}_i$, when these are distributed at random $1/N\Sigma_i f(\vec{n}_i)\to\int(d^2\vec{n}/4\pi)f(\vec{n})\equiv\overline{f}$. For instance, for arbitrary $\vec{n}$-independent vectors $\vec{v}_1$ and $\vec{v}_2$, we have

$$\frac{1}{N}\sum_i(\vec{v}_1\cdot\vec{n}_i)(\vec{v}_2\cdot\vec{n}_i)\to\overline{(\vec{v}_1\cdot\vec{n}(\vec{v}_2\cdot\vec{n})}=\tfrac{1}{3}\vec{v}_1\cdot\vec{v}_2. \tag{A13}$$

APPENDIX B: GENERAL FORMULAS FOR THE COEFFICIENTS OF THE SUSCEPTIBILITY

The general expression for the equilibrium linear susceptibility is given by Eq. (3.1) with the following expressions for the coefficients:

$$a_0=\frac{1}{N}\sum_i \vec{h}\cdot\mathbf{\Gamma}_i\cdot\vec{h},$$

$$a_1=\frac{1}{N}\sum_i\sum_{j\neq i}\vec{h}\cdot(\mathbf{\Gamma}_i\cdot\mathbf{G}_{ij}\cdot\mathbf{\Gamma}_j)\cdot\vec{h},$$

$$\begin{aligned}a_2=&-\frac{2}{N}\sum_i\sum_{j\neq i}\vec{h}\cdot(\mathbf{\Gamma}_i\cdot\mathbf{G}_{ij}\cdot\mathbf{\Gamma}_j\cdot\mathbf{G}_{ij}\cdot\mathbf{\Gamma}_i)\cdot\vec{h}+\frac{2}{N}\sum_i\sum_{j\neq i}\sum_{k\neq j}\vec{h}\cdot(\mathbf{\Gamma}_i\cdot\mathbf{G}_{ij}\cdot\mathbf{\Gamma}_j\cdot\mathbf{G}_{jk}\cdot\mathbf{\Gamma}_k)\cdot\vec{h}\\&+\frac{1}{N}\sum_i\sum_{j\neq i}\left\{\frac{1-S_2}{r_{ij}^6}[(\vec{h}\cdot\mathbf{\Lambda}_i\cdot\vec{h})(\hat{r}_{ij}\cdot\mathbf{\Lambda}_i\cdot\hat{r}_{ij})+2(\vec{h}\cdot\mathbf{\Lambda}_i\cdot\hat{r}_{ij})^2+\Omega(\vec{h}\cdot\vec{n}_i)^2(\vec{n}_i\cdot\hat{r}_{ij})^2]\right.\\&\left.+S_2[(\vec{h}\cdot\mathbf{\Lambda}_i\cdot\vec{h})(\vec{n}_j\cdot\mathbf{G}_{ij}\cdot\mathbf{\Lambda}_i\cdot\mathbf{G}_{ij}\cdot\vec{n}_j)+2(\vec{h}\cdot\mathbf{\Lambda}_i\cdot\mathbf{G}_{ij}\cdot\vec{n}_j)^2+\Omega(\vec{h}\cdot\vec{n}_i)^2(\vec{n}_i\cdot\mathbf{G}_{ij}\cdot\vec{n}_j)^2]\right\}\\&-\frac{1}{N}\sum_i\sum_{j\neq i}(\vec{h}\cdot\mathbf{\Gamma}_i\cdot\vec{h})\left[\frac{1-S_2}{r_{ij}^6}(\hat{r}_{ij}\cdot\mathbf{\Gamma}_i\cdot\hat{r}_{ij})+S_2(\vec{n}_j\cdot\mathbf{G}_{ij}\cdot\mathbf{\Gamma}_i\cdot\mathbf{G}_{ij}\cdot\vec{n}_j)\right],\end{aligned}$$

where $\mathbf{G}_{ij}$, $\vec{r}_{ij}$, and $\hat{r}_{ij}$ are defined in Eq. (2.3), and $\mathbf{\Gamma}$, $\mathbf{\Lambda}$, and Ω in Eqs. (A4) and (A5) and also involve the $S_l(\sigma)$.

When calculating these coefficients, the same type of averages appear as in the isotropic case (see Refs. 3 and 12 for details of the calculation) and with the same multiplicities. The only difference is the weight function and hence the formulas required to calculate those averages [Eqs. (A1) and (A2) instead of Eqs. (A11) and (A12)].

APPENDIX C: GENERAL FORMULA FOR THE COEFFICIENT B_2 OF THE SPECIFIC HEAT

In the general expression (3.9) for the specific heat the coefficient b_0 is given by Eq. (3.10), while b_2 reads

$$\begin{aligned}Nb_2=&\tfrac{1}{3}\{2(1-S_2)-4\sigma S_2'-\sigma^2S_2''\}\sum_i\sum_{j\neq i}r_{ij}^{-6}\\&+\tfrac{1}{2}\{2S_2(1-S_2)+4\sigma S_2'(1-2S_2)\\&+\sigma^2[S_2''(1-2S_2)-2(S_2')^2]\}\sum_i\sum_{j\neq i}r_{ij}^{-6}\\&\times[(\hat{r}_{ij}\cdot\vec{n}_i)^2+(\hat{r}_{ij}\cdot\vec{n}_j)^2]+\{S_2^2+4\sigma S_2S_2'\\&+\sigma^2[S_2S_2''+(S_2')^2]\}\sum_i\sum_{j\neq i}(\vec{n}_i\cdot\mathbf{G}_{ij}\cdot\vec{n}_j)^2,\end{aligned}\tag{C1}$$

where $f'=df/d\sigma$. An arbitrary S_l' can be expressed in terms of averaged Legendre polynomial by means of the following differential-recurrence relation:

$$\begin{aligned}\frac{dS_l}{d\sigma}=&\frac{(l-1)l}{(2l-1)(2l+1)}S_{l-2}+\frac{2l(l+1)}{3(2l-1)(2l+3)}S_l\\&+\frac{(l+1)(l+2)}{(2l+1)(2l+3)}S_{l+2}-\frac{2}{3}S_2S_l.\end{aligned}\tag{C2}$$

This useful formula can readily be demonstrated by taking the derivative of the definition of $S_l\equiv\langle P_l\rangle_{\rm a}=\int_{-1}^{1}dz\,P_le^{\sigma z^2}/\int_{-1}^{1}dz\,e^{\sigma z^2}$:

$$\begin{aligned}\frac{dS_l}{d\sigma}&=\frac{\int_{-1}^{1}dz\,z^2P_le^{\sigma z^2}}{\int_{-1}^{1}dz\,e^{\sigma z^2}}-\frac{\int_{-1}^{1}dz\,P_le^{\sigma z^2}\int_{-1}^{1}dz\,z^2e^{\sigma z^2}}{(\int_{-1}^{1}dz\,e^{\sigma z^2})^2}\\&=\langle z^2P_l\rangle_{\rm a}-\tfrac{1}{3}S_l(1+2S_2),\end{aligned}\tag{C3}$$

where $\langle z^2\rangle_{\mathrm{a}}=(1+2S_2)/3$ has been used. The product of P_l with z can be expanded in Legendre polynomials by using the corresponding relation for associated Legendre functions P_l^m (Ref. 24, Chap. 12),

$$zP_l=\frac{1}{2l+1}[lP_{l-1}+(l+1)P_{l+1}]. \tag{C4}$$

Multiplying zP_l by z, using again Eq. (C4) to expand $zP_{l\pm 1}$ on the right-hand side, and gathering terms yields

$$z^2P_l=\frac{(l-1)l}{(2l-1)(2l+1)}P_{l-2}+\frac{2l(l+1)-1}{(2l-1)(2l+3)}P_l+\frac{(l+1)(l+2)}{(2l+1)(2l+3)}P_{l+2}.$$

Averaging this result and substituting in Eq. (C3), we finally get the desired Eq. (C2).

APPENDIX D: MONTE CARLO SIMULATIONS

In order to obtain nonperturbative results to test the analytical expressions we have performed careful Monte Carlo simulations, by a method similar to that employed in Ref. 26. The trial Monte Carlo step (MCS) is a random rotation of the spin within a cone, achieved by generating a random vector with uniform probability on the surface of a sphere of radius ϱ, adding the random vector to the initial spin, and finally normalizing the resulting vector. For a better acceptance ratio of the generated configurations, we scale that radius with T as $\varrho=0.7/\sqrt{\sigma}$.

In terms of the maximum anisotropy field $\mu_0H_K=2A/m$, where A is the anisotropy parameter and m is the magnetic moment, a dimensionless probing field can be defined as $\Delta H/H_K$ or, in temperature units, as $\Delta\xi=2\sigma\Delta H/H_K$. The latter is the argument in the Langevin function for the (isotropic) magnetization, and it controls if the response is linear in ΔH. Therefore to treat all the temperatures on the same footing $\Delta\xi\propto\Delta H/T$ is kept constant in the simulation ($\Delta\xi=0.15$) which requires one to decrease the probing field with T. The value $\Delta\xi=0.15$ used should ensure linear response since it is well below the values $\Delta\xi=0.3$–0.5, where nonlinear terms can start to contribute appreciably to the equilibrium response (see, for instance, Appendix C of Ref. 27).

The number of dipoles in each simulation is indicated in the panels of Fig. 1 and the simulations are done with open boundary conditions. The absolute value of the coefficient in front of Eq. (2.2) can be written as $2A\,h_{\mathrm{d}}$, so that h_{d} [Eq. (2.7)] is used as the input in the simulation. In order to control that the response is the equilibrium one, we apply a sinusoidal probing field of low frequency ($f=8\times10^{-6}$ MCS^{-1}) and check that further reducing f does not change the results. Besides, the ten first periods are excluded from the average and the susceptibility sampled over the 20 following periods.

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$$F_1=G_1-\langle G_1\rangle_{\mathrm{a}},$$

$$F_2=G_2-\langle G_2\rangle_{\mathrm{a}}-2\langle G_1\rangle_{\mathrm{a}}[G_1-\langle G_1\rangle_{\mathrm{a}}].$$

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