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The random dipolar-field approximation for systems of interacting magnetic particles

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The dipolar interaction is known to play an important role on the magnetic properties of small magnetic particles. For moderate concentrations the most noticeable effect is an increase of the relaxation time, whereas for sufficiently dense systems some degree of correlational order may be observed. In this paper, a mean-field approximation is introduced to correctly account for these changes. It is based on the interpretation of the dipolar field, produced by an ensemble of particles, as a random field acting on a reference particle. This field contains the statistical moments of the magnetisation of the reference particle and is computed assuming a random spatial distribution of the particles. The result is a new term in the free energy of the reference particle, expressed as a cumulant expansion of the random field, carried up to fourth-order. This model correctly predicts both the increase in the relaxation time and a phase transition to a ferromagnetic state for sufficiently dense systems. The dynamics is also studied by introducing this new free energy into the Fokker-Planck equation for the single-particle magnetic moment. The result is a non-linear Fokker-Planck equation, which is solved numerically to illustrate the divergence of the relaxation time at the phase transition. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4802583]

I. INTRODUCTION

Fine magnetic particles continue to be a subject of intensive experimental and theoretical research, motivated by their interesting magnetic properties[1–4] and their potential for several applications.[5–7] Much of this interest stems from their reduced dimensions, which bring about two unique and important properties. First, it inhibits the formation of magnetic domains, inducing the spins to behave in unison as a single magnetic dipole. Second, it shallows the potential barrier that separates the stable energy minima, leading to a strong dependence of the system on both temperature and the relaxation time. The problem is therefore dynamical in nature and relevant only at finite temperatures. On the other hand, the absence of physical contact between the particles implies that they may only interact via the dipole-dipole interaction. Thus, a sufficiently diluted sample will approximately behave as a non-interacting ensemble, which greatly simplifies the problem. The dynamics of the magnetisation may be described using (for instance) Brown's stochastic description of the Landau-Lifshitz-Gilbert equation.[4,8,9] This approach has been extremely successful, leading to considerable progress in the understating of the thermo-magnetic properties of fine particles.[10–19]

Neglecting the dipole-dipole interaction, however, is not always a good approximation. Several experiments[20–25] have unambiguously demonstrated that common practical situations encountered in the laboratory can seldom be regarded as "sufficiently diluted." This is a consequence of the large magnetic moment of the particles, usually orders of magnitude higher than that of ordinary paramagnets. The effects of the dipolar interaction manifest themselves in different ways, depending on the particle concentration:[26] upon increasing it from an infinitely diluted state, one first observes a change in the relaxation time (related to the anisotropy barrier), followed by the appearance of some degree of orientational correlation and finally reaching an ordered state with a non-zero net magnetisation even at zero field. The importance of this interaction was well illustrated in Ref. 21, where AC susceptibility was used to study the effective energy barrier of Ni nanoparticles embedded in an amorphous SiO_2/C matrix at different concentrations. The authors observed astounding 35% and 75% increases in the effective barrier, with respect to a sufficiently diluted system, for samples with 7.9 and 12.8 wt.%, respectively.

Unfortunately, introducing the dipolar interaction in a theoretical framework is an extremely complex task. It invariably results in a many-body problem, for which few techniques have been developed. All single-particle techniques are rendered useless and even the simplest of calculations become extremely involved.

Numerical studies of dipole-interacting systems are also challenging, due mainly to three reasons. First, the interaction is of long-range, thus scaling faster than $O(N)$, where N is the number of particles: in principle it scales as $O(N)^2$, which can be reduced to $O(N \log N)$ using fast Fourier transform methods[27] and further to $O(N)$ (albeit with a high multiplier) using multipole expansions.[28] Second, the dipolar interaction has a reduced symmetry. This means that the properties of systems containing only a handful of particles[14] are not guaranteed to reflect, *a priori*, those of larger (and thus more realistic) samples. The same is true for simple geometries, such as chains[29] or layers of particles. Finally, unlike bulk magnets where thermal fluctuations can be omitted in certain circumstances, the strong temperature dependence of small particles entails that all simulations must be of

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statistical nature. This means either Monte Carlo[30–34] or the direct solution[12,18] of the aforementioned stochastic equations.[4,8,9] The former, albeit usually more efficient than the latter, suffers from a ill defined time-step, thus making the stochastic approach physically more meaningful (for an alternative see Ref. 35).

In view of the aforementioned difficulties, in order to advance in the understanding of dipole-interacting systems some type of approximation is required. Equilibrium properties have successfully been treated using thermodynamic perturbation theory.[36,37] As for the dynamics, one must invariably reduce the problem back to that of a single-particle, where a plethora of techniques has already been developed (a good example is the use of Kramers escape rate theory[8,9,38] to compute the relaxation time). This is a form of mean-field approximation and bears some resemblance to the Curie-Weiss theory of ferromagnetism. However, a fundamental difference exists; namely, that the first manifestation of the dipolar interaction is not to incite some degree of order in the system, but rather to increase its effective anisotropy barrier.[21,22] This leads to the so called Vogel-Fulcher modification of the relaxation time.[39,40] In other words, orientational correlations that lead to spin-glass or ordered states are corrections of higher order, unlike in the Curie-Weiss theory.

Two important contributions in this direction were recently given by Felderhof and Jones,[41] and Dejardin.[42] They introduced the mean-field approximations into the dynamics of the problem via an effective field appearing in the Fokker-Planck equation. The result is a non-linear (in the distribution function) Fokker-Planck equation, which reduces to the original in the limit of infinite dilution. Felderhof and Jones, however, did not include the fundamental effects of anisotropy, as Dejardin did.

It is possible to give the following arguments about a mean-field approximation. The focus lies on a reference particle whose free energy in the limit of infinite dilution is U. The introduction of the dipolar interaction is tantamount to adding a new term U_{dip}, constructed such that it becomes negligible in the limit of infinite dilution. Moreover, besides depending on the magnetisation of the reference particle, it may also depend on its statistical moments. The reason being that it implicitly contains a sum over the magnetisation vectors of all other particles in the sample. But, since all particles are indistinguishable, this sum can be replaced by the average magnetisation of the reference particle. The effective field, which is the gradient of the free energy, will then depend on these averages as well. Whence, introducing it in the Fokker-Planck equation will make it non-linear; the same is true for the equations dictating the time evolution of the statistical moments.

In this paper, I will present a mean-field approximation devised to meet these criteria. This will be accomplished by treating the dipolar field, acting on a reference particle due to all particles in the sample, as a random field, an approximation which will be justified in Sec. II. The new terms will come about in the form of a cumulant expansion of this random field containing the aforementioned expectations, as developed in Secs. III and IV. The main premise in devising the approximation will be to exploit the random spatial arrangement of particles usually encountered in real systems. In Sec. V, it will be shown that this model correctly predicts for the first correction an increase in the effective anisotropy barrier. Further increase of the dipolar interaction also leads to a phase transition toward an ordered state, the properties of which are the subject of Sec. VI. This transition is equivalent to a divergence of the relaxation time, also predicted by Dejardin in Ref. 42, and which will be studied via the new non-linear Fokker-Planck equation developed in Sec. VII. Discussions and conclusions are given in Sec. VIII.

II. CONSTRUCTION OF THE EFFECTIVE FREE ENERGY

Consider a system of N magnetic particles with magnetic moments μ_s and magnetisation orientation $\boldsymbol{m}_s = (m_{s1}, m_{s2}, m_{s3})$, where $|\boldsymbol{m}_s| = 1$ and $s = 1, 2, \ldots, N$. The total free energy of the system may be written as

$$\mathcal{E} = \sum_{s=1}^{N} U_s(\boldsymbol{m}_s) + \sum_{\substack{s=1 \\ r>s}}^{N} U_{sr}(\boldsymbol{m}_s, \boldsymbol{m}_r), \tag{1}$$

where $U_s(\boldsymbol{m}_s)$ represent the single-particle free energies comprising, for instance, anisotropy terms or the Zeeman interaction with an external field. The second term refers to the dipole-dipole interactions and may be written as the quadratic form

$$U_{sr}(\boldsymbol{m}_s, \boldsymbol{m}_r) = -\boldsymbol{m}_s^{\mathrm{T}} \mathcal{D}_{sr} \boldsymbol{m}_r, \tag{2}$$

where T stands for transpose and $\mathcal{D}_{sr}$ is the dipolar-interaction tensor between particles s and r

$$\mathcal{D}_{sr} = \mu_s \mu_r \left(\frac{\mu_0}{4\pi}\right) \left(\frac{3\boldsymbol{e}_{sr}\boldsymbol{e}_{sr}^{\mathrm{T}} - I}{R_{sr}^3}\right). \tag{3}$$

Here R_{sr} and $\boldsymbol{e}_{sr}$ are, respectively, the distance and the unit vector between particles s and r; I is the 3×3 identity matrix and μ_0 is the permeability of free space. In equilibrium, the probability density function $f(\boldsymbol{m}_1, \ldots, \boldsymbol{m}_N)$ for the N-particle system is given by the Maxwell-Boltzmann formula

$$f(\boldsymbol{m}_1, \ldots, \boldsymbol{m}_N) = \frac{e^{-\beta\mathcal{E}}}{\int e^{-\beta\mathcal{E}}\, \mathrm{d}\boldsymbol{m}_1 \ldots \mathrm{d}\boldsymbol{m}_N}, \tag{4}$$

where $\beta = 1/k_B T$, each integral begin over a unit sphere.

Now focus on a single particle, e.g., $\boldsymbol{m}_1$. Integrating over $\boldsymbol{m}_2, \ldots, \boldsymbol{m}_N$, we obtain the marginal distribution

$$f(\boldsymbol{m}_1) = \frac{e^{-\beta U_1(\boldsymbol{m}_1)}\Omega(\boldsymbol{m}_1)}{\int e^{-\beta U_1(\boldsymbol{m}_1)}\Omega(\boldsymbol{m}_1)\, \mathrm{d}\boldsymbol{m}_1}, \tag{5}$$

where

$$\Omega(\boldsymbol{m}_1) = \int \exp\left\{ -\beta \sum_{s=2}^{N} U_s - \beta \sum_{\substack{s=1 \\ r>s}}^{N} U_{sr} \right\} \mathrm{d}\boldsymbol{m}_2 \ldots \mathrm{d}\boldsymbol{m}_N. \tag{6}$$

Equation (5) is an exact result in the sense that, if it were possible to compute $\Omega(\boldsymbol{m}_1)$, it would give the distribution of particle 1, irrespective of the behaviour of the other particles.

Next, define the (dimensionless) dipolar field $\boldsymbol{\xi}$ of all other particles acting on $\boldsymbol{m}_1$

$$\boldsymbol{\xi} = \beta \sum_{r=2}^{N} \mathcal{D}_{1r} \boldsymbol{m}_r. \tag{7}$$

Also, change integration variables in Eq. (6), from $\{\boldsymbol{m}_2, \boldsymbol{m}_3, \ldots, \boldsymbol{m}_N\}$ to $\{\boldsymbol{\xi}, \boldsymbol{m}_3, \ldots, \boldsymbol{m}_N\}$. This transformation is one-to-one and the Jacobian is a constant, which will eventually cancel in Eq. (5), since it will also appear in the denominator. Thus, we may write Eq. (6) as

$$\Omega(\boldsymbol{m}_1) = \int \Lambda(\boldsymbol{\xi}) e^{\boldsymbol{m}_1^{\mathrm{T}} \boldsymbol{\xi}} \, \mathrm{d}\boldsymbol{\xi}, \tag{8}$$

where

$$\Lambda(\boldsymbol{\xi}) = \int \exp\left\{ -\beta \sum_{s=2}^{N} U_s - \beta \sum_{\substack{s=2 \\ r>s}}^{N} U_{sr} \right\} \mathrm{d}\boldsymbol{m}_3 \ldots \mathrm{d}\boldsymbol{m}_N, \tag{9}$$

with $\boldsymbol{m}_2$ taken to be a function of $\boldsymbol{\xi}, \boldsymbol{m}_3, \ldots, \boldsymbol{m}_N$.

Alternatively, we could also write the joint distribution of $\boldsymbol{m}_1$ and $\boldsymbol{\xi}$ as

$$f(\boldsymbol{m}_1, \boldsymbol{\xi}) = \frac{e^{-\beta U_1(\boldsymbol{m}_1) + \boldsymbol{m}_1^{\mathrm{T}} \boldsymbol{\xi}} \Lambda(\boldsymbol{\xi})}{\int e^{-\beta U_1(\boldsymbol{m}_1) + \boldsymbol{m}_1^{\mathrm{T}} \boldsymbol{\xi}} \Lambda(\boldsymbol{\xi}) \, \mathrm{d}\boldsymbol{m}_1 \, \mathrm{d}\boldsymbol{\xi}}. \tag{10}$$

Marginalising over $\boldsymbol{m}_1$ then yields the equilibrium distribution of $\boldsymbol{\xi}$

$$f(\boldsymbol{\xi}) = \frac{\Lambda(\boldsymbol{\xi}) \Gamma(\boldsymbol{\xi})}{\int \Lambda(\boldsymbol{\xi}) \Gamma(\boldsymbol{\xi}) \, \mathrm{d}\boldsymbol{\xi}}, \qquad \Gamma(\boldsymbol{\xi}) = \int e^{-\beta U_1(\boldsymbol{m}_1) + \boldsymbol{m}_1^{\mathrm{T}} \boldsymbol{\xi}} \, \mathrm{d}\boldsymbol{m}_1. \tag{11}$$

Now comes the first approximation: it is possible to argue that the contribution of $\Gamma(\boldsymbol{\xi})$ (i.e., of $\boldsymbol{m}_1$) to the distribution $f(\boldsymbol{\xi})$ is minuscule compared with that of all other particles appearing implicitly in $\Lambda(\boldsymbol{\xi})$. Hence, we shall take $\Gamma(\boldsymbol{\xi}) \sim 1$ and discard it entirely from Eq. (11). In this case, it is possible to conclude that the function $\Lambda(\boldsymbol{\xi})$ can, apart from a normalisation constant, be interpreted as the distribution function of $\boldsymbol{\xi}$. Whence, Eq. (8) may be written as an average over this random field $\boldsymbol{\xi}$

$$\Omega(\boldsymbol{m}_1) \sim \langle e^{\boldsymbol{m}_1^{\mathrm{T}} \boldsymbol{\xi}} \rangle.$$

The normalisation constant is again irrelevant, since it can be factored out in Eq. (5). Thus, omitting the suffix 1, we may finally write the single-particle distribution function as

$$f(\boldsymbol{m}) = \frac{1}{Z} \exp\left\{ -\beta U(\boldsymbol{m}) + \log\langle e^{\boldsymbol{m}^{\mathrm{T}} \boldsymbol{\xi}} \rangle \right\}, \tag{12}$$

where Z is the partition function

$$Z = \int \exp\{ -\beta U(\boldsymbol{m}) + \log\langle e^{\boldsymbol{m}^{\mathrm{T}} \boldsymbol{\xi}} \rangle \} \, \mathrm{d}\boldsymbol{m}. \tag{13}$$

From Eq. (12), it is possible to identify the mean-field effective energy

$$\mathcal{U}_{\mathrm{eff}}(\boldsymbol{m}) = U(\boldsymbol{m}) - \frac{1}{\beta} \log\langle e^{\boldsymbol{m}^{\mathrm{T}} \boldsymbol{\xi}} \rangle. \tag{14}$$

III. CUMULANT EXPANSION OF THE DIPOLAR FIELD

The second term in the right-hand side of Eq. (14) is the cumulant generating function of $\boldsymbol{\xi}$ with parameter $\boldsymbol{m}$. Thus, it is possible to perform a series expansion written in terms of the cumulants Θ of $\boldsymbol{\xi}$. Using Einstein's sum convention, this may be written as

$$\log\langle e^{\boldsymbol{m}^{\mathrm{T}} \boldsymbol{\xi}} \rangle = m_i \Theta_i + \frac{1}{2!} m_i m_j \Theta_{ij} + \frac{1}{3!} m_i m_j m_k \Theta_{ijk} + \ldots, \tag{15}$$

where $i, j, k = 1, 2, 3$. The cumulants are related to the moments by the following expressions:

$$\Theta_i = \langle \xi_i \rangle, \tag{16}$$

$$\Theta_{ij} = \langle \xi_i \xi_j \rangle - \langle \xi_i \rangle \langle \xi_j \rangle, \tag{17}$$

$$\Theta_{ijk} = \langle \xi_i \xi_j \xi_k \rangle - \langle \xi_i \xi_j \rangle \langle \xi_k \rangle [3] + 2 \langle \xi_i \rangle \langle \xi_j \rangle \langle \xi_k \rangle, \tag{18}$$

$$\begin{aligned} \Theta_{ijk\ell} = {} & \langle \xi_i \xi_j \xi_k \xi_\ell \rangle - \langle \xi_i \xi_j \xi_k \rangle \langle \xi_\ell \rangle [4] - \langle \xi_i \xi_j \rangle \langle \xi_k \xi_\ell \rangle [3] \\ & + 2 \langle \xi_i \xi_j \rangle \langle \xi_k \rangle \langle \xi_\ell \rangle [6] - 6 \langle \xi_i \rangle \langle \xi_j \rangle \langle \xi_k \rangle \langle \xi_\ell \rangle. \end{aligned} \tag{19}$$

In these equations, the quantities inside brackets indicate a sum over distinct partitions with the same block sizes. For instance,

$$\langle \xi_i \xi_j \rangle \langle \xi_k \rangle [3] = \langle \xi_i \xi_j \rangle \langle \xi_k \rangle + \langle \xi_i \xi_k \rangle \langle \xi_j \rangle + \langle \xi_j \xi_k \rangle \langle \xi_i \rangle.$$

More generally, an arbitrary cumulant is a sum over all possible distinct products of moments, each multiplied by a coefficient $(-1)^{k-1}(k-1)$, where k is the number of blocks in each term.

Henceforth, we will consider a reference particle with magnetic moment μ and magnetisation orientation $\boldsymbol{m}$, located at the origin of the coordinate system. The random field $\boldsymbol{\xi}$ stems from the dipolar field created by N other particles, whose distances and unit vectors with respect to the origin are R_s and $\boldsymbol{e}_s$, respectively. According to Eq. (7), $\boldsymbol{\xi}$ may be written as

$$\boldsymbol{\xi} = \sum_{s=1}^{N} \boldsymbol{X}_s, \tag{20}$$

where

$$\boldsymbol{X}_s = \beta \mu \mu_s \left(\frac{\mu_0}{4\pi} \right) \frac{1}{R_s^3} \left(3 \boldsymbol{e}_s \boldsymbol{e}_s^{\mathrm{T}} - I \right) \boldsymbol{m}_s. \tag{21}$$

Up to this point nothing has been said about the spatial arrangement of the particles. To continue, it is useful to exploit the fact that in most real systems, such as powder samples or colloidal suspensions, the particles are randomly dispersed in space. Thus, the vectors $\boldsymbol{X}$ will be treated as random variables and, according to Eq. (21), they are themselves combinations of several other random variables: (i) the distance R_s of particle s from the origin, (ii) the unit vector $\boldsymbol{e}_s$, (iii) the magnetic moment μ_s, and (iv) the magnetisation $\boldsymbol{m}_s$. The magnetic moment μ of the reference particle is assumed to be known, which is equivalent to saying that, if we were to average a product such as $\mu_s \mu_r$ then, since the magnetic moments are independent, $\langle \mu_s \mu_r \rangle = \langle \mu_s \rangle \langle \mu_r \rangle$. Except for the magnetisation $\boldsymbol{m}_s$, all other random variables are independent from one particle to another—i.e., they are independent identically distributed (iid) random variables. As for the magnetisation of each particle, they certainly need not be independent. However, it is possible to argue as follows: if the particles have a uniaxial (or some other type) of anisotropy, then the orientation of each magnetic moment will be dictated, mostly, by the direction of the easy axis which, from one particle to another, is an iid random variable. Thus, as the next approximation, we shall take that $\langle m_{si} m_{rj} \rangle = \langle m_{si} \rangle \langle m_{rj} \rangle$ when $r \neq s$. Since the particles in the sample are indistinguishable this is in turn simply $\langle m_i \rangle \langle m_j \rangle$, the moments of the reference particle. Below it will be shown that, since the unit vectors $\boldsymbol{e}$ are iid, the correlations in the magnetisation shall appear only in the fourth cumulant of the expansion (15).

From Eq. (20), it is then possible to conclude that $\boldsymbol{\xi}$ is a sum of iid random variables. Its cumulants are, therefore, N times the cumulants of $\boldsymbol{X}$ (since they are iid we may drop the suffix s). The unit vectors $\boldsymbol{e}$ are assumed to be uniformly distributed over the unit sphere (isotropic distribution). Thus, in deriving the cumulants of $\boldsymbol{X}$ their averages will be computed explicitly, while all others will be left unspecified for the moment. Let us define the dimensionless quantities

$$\eta_k = \left(\frac{\beta \mu \mu_0}{4\pi} \right)^k \langle \mu^k \rangle \left\langle \frac{1}{R^{3k}} \right\rangle. \tag{22}$$

Moreover, for simplicity of notation, define

$$q_{ij\ldots\ell} = \langle m_i m_j \ldots m_\ell \rangle, \tag{23}$$

i.e., $q_i = \langle m_i \rangle$, $q_{ij} = \langle m_i m_j \rangle$, etc.

The first cumulant is the mean. Taking the expectation of Eq. (21) and using that $\langle e_i e_j \rangle = (1/3)\delta_{ij}$, we find

$$\Theta_i = \langle \xi_i \rangle = N \langle X_i \rangle = 0. \tag{24}$$

This result requires only an average over the $\boldsymbol{e}$; it is thus true irrespective of the value of the magnetisation and follows from the isotropy of space. It also greatly simplifies Eqs. (16)–(19).

The calculation of the second, third, and fourth order cumulants is straightforward, albeit cumbersome. One needs simply multiply out the terms that appear when we take products of $\boldsymbol{X}$ and then average over $\boldsymbol{e}$. The second cumulant will contain terms of the form $\langle X_i^2 \rangle$ and $\langle X_i X_j \rangle$. The result is

$$\Theta_{ij} = \frac{N\eta_2}{5} [3\delta_{ij} + q_{ij}], \tag{25}$$

where δ_{ij} is the Kronecker's delta. For the third cumulant there are three characteristic terms; namely $\langle X_i^3 \rangle$, $\langle X_i^2 X_j \rangle$, and $\langle X_i X_j X_k \rangle$. The results can be written compactly as

$$\begin{aligned} \Theta_{ijk} &= \frac{2N\eta_3}{35} [3\delta_{ij} q_k[3] - q_{ijk}] \\ &= \frac{2N\eta_3}{35} \begin{cases} 9q_i - q_{iii} & \text{if } i = j = k, \\ 3q_k - q_{iik} & \text{if } i = j \neq k, \\ -q_{ijk} & \text{if } i \neq j \neq k. \end{cases} \end{aligned} \tag{26}$$

The fourth-order cumulant, according to Eq. (19), is the first where two different types of terms appear, namely $\langle X_i X_j X_k X_\ell \rangle$ and $\langle X_i X_j \rangle \langle X_k X_\ell \rangle [3]$. After a cumbersome computation, we obtain the result

$$\begin{aligned} \Theta_{ijk\ell} = {} & \frac{3N\eta_4}{35} \{ 3\delta_{ij}\delta_{k\ell}[3] + \delta_{ij} q_{k\ell}[6] + q_{ijk\ell} \} \\ & - \frac{3N\eta_2^2}{25} \left\{ 3\delta_{ij}\delta_{k\ell}[3] + \delta_{ij} q_{k\ell}[6] + \frac{1}{3} q_{ij} q_{k\ell}[3] \right\}, \end{aligned} \tag{27}$$

or

$$\Theta_{ijk\ell} = \begin{cases} \dfrac{3N\eta_4}{35}[9 + 6q_{ii} + q_{iiii}] & -\dfrac{3N\eta_2^2}{25}[9 + 6q_{ii} + q_{ii}^2] & \text{if } i = j = k = \ell, \\ \dfrac{3N\eta_4}{35}[3 + q_{ii} + q_{kk} + q_{iikk}] & -\dfrac{3N\eta_2^2}{25}\left[3 + q_{ii} + q_{kk} + \dfrac{q_{ii}q_{kk} + 2q_{ik}^2}{3}\right] & \text{if } i = j \neq k = \ell, \\ \dfrac{3N\eta_4}{35}[3q_{i\ell} + q_{iii\ell}] & -\dfrac{3N\eta_2^2}{25}[3q_{i\ell} + q_{ii}q_{i\ell}] & \text{if } i = j = k \neq \ell, \\ \dfrac{3N\eta_4}{35}[q_{k\ell} + q_{iik\ell}] & -\dfrac{3N\eta_2^2}{25}\left[q_{k\ell} + \dfrac{q_{ii}q_{k\ell} + 2q_{ik}q_{i\ell}}{3}\right] & \text{if } i = j \neq k \neq \ell. \end{cases} \tag{28}$$

This completes the problem. Both the equilibrium distribution $f(\boldsymbol{m})$ in Eq. (12) and the effective free energy $\mathcal{U}_{\text{eff}}(\boldsymbol{m})$ in Eq. (14) can be written in terms of the m_i and the q's, by substituting Eqs. (24)–(27) in Eq. (15). For this reason, we will also eventually write $f(\boldsymbol{m}, q)$ and $\mathcal{U}_{\text{eft}}(\boldsymbol{m}, q)$ for these quantities. In total, there are 3 coefficients q_i of first order; 6 coefficients q_{ij} of second order; 10 coefficients q_{ijk} of third order; and 15 coefficients $q_{ijk\ell}$ of fourth order.

The new equilibrium distribution depends, itself, on the moments of the magnetisation. Thus, they must be determined by the self-consistency relation,

$$q_{ij\ldots\ell} = \int m_i m_j \ldots m_\ell f(\boldsymbol{m}; q)\, \mathrm{d}\boldsymbol{m}. \tag{29}$$

This is a nonlinear equation which must be solved simultaneously for the statistical moments of the magnetisation, q. The root-finding can be accomplished using Newton's method.[43] The integral on the right-hand side is performed over the unit sphere and can be efficiently computed using Lebedev quadrature.[44]

Now assume, conversely, that the $\boldsymbol{m}_s$ (and thence the $\boldsymbol{X}_s$) were not independent. Then, we should instead perform a cumulant expansion in $\boldsymbol{\xi}$ directly. The first order cumulant is again zero. In the second order cumulant, e.g., $\langle \xi_1^2 \rangle$, there will appear N terms of the form $\langle X_{s1}^2 \rangle$, as before. In addition, there will be many other terms of the form $\langle X_{s1} X_{r1} \rangle$ with $r \neq s$. Now, let $\langle\rangle_{\boldsymbol{e}}$ and $\langle\rangle_{\boldsymbol{m}}$ denote averages over $\boldsymbol{e}$ and $\boldsymbol{m}$, respectively. Then $\langle X_{s1} X_{r1} \rangle_{\boldsymbol{e},\boldsymbol{m}} = \langle \langle X_{s1} \rangle_{\boldsymbol{e}} \langle X_{r1} \rangle_{\boldsymbol{e}} \rangle_{\boldsymbol{m}}$. The average over $\boldsymbol{e}$ is, by itself, always zero. Thus, even if the magnetizations $\boldsymbol{m}_s$ were dependent, this would make no difference on the second order cumulants due to the independence of the $\boldsymbol{e}$. Similarly, for the third order cumulant, for instance $\langle \xi_1^3 \rangle$, there will be terms of the form $\langle X_{s1}^2 X_{r1} \rangle$ and $\langle X_{s1} X_{r1} X_{p1} \rangle$. For the same reasons, all these extra terms are again zero. It is only when we reach the fourth order cumulant that the dependence of the $\boldsymbol{m}_s$ begins to play a role. This appears in the second term of Eq. (27) or Eq. (28) (proportional to η_2^2) and consists mainly in replacements of the type $\langle m_i^2 \rangle^2 \to \langle m_{si}^2 m_{ri}^2 \rangle$.

As a rough estimate of η_1, we may use the data of Ref. 22 for Ni nanoparticles: $\mu \sim 10^3 \mu_B$, where μ_B is the Bohr magnetron, and $R \sim 20$ nm. For $T = 300$ K, we find $\eta_1 \sim 10^{-4}$. Notwithstanding the arbitrariness of these numbers, the main point is that it is reasonable to expect that $\eta_1 < 1$, in which case the coefficients $\eta_2, \eta_3, \ldots,$ form a decreasing sequence. This guarantees a rapid convergence of the series (15), hence, corroborating the validity of the present model. On the other hand, one should note that the product $N\eta_k$ may very well be higher than unity.

It is possible to give a physical interpretation to combinations such as $N\eta_2$, appearing for instance in Eq. (25). It is customary to assume that the average inter-particle distance is proportional to the particle density $n = N/V$, where V is the total volume of the sample; i.e., $\langle R \rangle \sim n^{-1/3}$. Therefore, the coefficient of the second-order cumulant will scale as $\sim Nn^2 = Vn^3$. Thus, if we take a system with a fixed density and increase the total volume, the net dipolar interaction will also increase. This non-extensivity is a direct consequence of the long-range nature of the dipolar interaction. Of course, it is also important to note that it depends much more strongly on n than on V.

IV. AXIALLY SYMMETRIC POTENTIALS

For definiteness, let us assume that the original free energy of the particle reads

$$-\beta U(\boldsymbol{m}) = \sigma m_z^2 + 2\sigma \boldsymbol{m}^{\mathrm{T}} \boldsymbol{h}, \tag{30}$$

where

$$\sigma = \frac{Kv}{k_B T}, \quad \boldsymbol{h} = \frac{\mu \boldsymbol{H}_{\mathrm{ext}}}{2Kv}, \tag{31}$$

K is the uniaxial anisotropy constant (with easy axis in the z-direction), v is the volume of the particle, and $\boldsymbol{H}_{\mathrm{ext}}$ is an externally applied field.

The coefficients q must reflect the symmetries contained in the unperturbed free energy of the reference particle. For instance, if the external field is zero and $\sigma \neq 0$, then all coefficients must not only depend exclusively on m_z but must also be invariant with respect to inversions. In this section, it will be shown how the entire scheme greatly simplifies in the event of axial symmetry, i.e., when $\boldsymbol{h} = h\boldsymbol{e}_3$. In this case, the following general comments can be said about the coefficients q [having in mind definition (23)].

For the first order coefficients, $q_1 = q_2 = 0$ and (in general) $q_3 \neq 0$. As for the second order, $q_{12} = q_{13} = q_{23} = 0$. Moreover, $q_{11} = q_{22}$ and $q_{11} + q_{22} = 1 - q_{33}$, which yields

$$q_{11} = q_{22} = \frac{1 - q_{33}}{2}.$$

Thus, the second order term in the cumulant expansion (15) is reduced to

$$\frac{1}{2!} m_i m_j \Theta_{ij} = \frac{N\eta_2}{10} \left(\frac{3q_{33} - 1}{2} \right) m_z^2. \tag{32}$$

The third order coefficients must satisfy $q_{111} = q_{222} = 0$ and $q_{333} \neq 0$. Furthermore,

$$q_{112} = q_{221} = q_{331} = q_{332} = q_{123} = 0.$$

Using $q_{113} = q_{223}$ and $q_{113} + q_{223} = q_3 - q_{333}$, we find

$$q_{113} = q_{223} = \frac{q_3 - q_{333}}{2}.$$

From these results, recalling the multiplicity of the terms appearing in the sum, we obtain

$$\frac{1}{3!} m_i m_j m_k \Theta_{ijk} = \frac{N\eta_3}{70} \left[(5q_3 + q_{333}) m_z + \left(q_3 - \frac{5}{3} q_{333} \right) m_z^3 \right]. \tag{33}$$

Finally, for the fourth-order coefficients, we must have $q_{1123} = q_{2213} = q_{3312} = 0$. The same is true of all coefficients q_{iiij} for $j \neq i$. From $q_{1133} = q_{2233}$ and $q_{1133} + q_{2233} = q_{33} - q_{3333}$, we find

$$q_{1133} = q_{2233} = \frac{q_{33} - q_{3333}}{2}.$$

We may also use that $q_{1111} = q_{2222}$ and $q_{1111} + q_{2222} + 2q_{1122} = 1 - 2q_{33} + q_{3333}$. Moreover, there is also the less intuitive relation that $3q_{1122} = q_{1111}$. Whence, we find that

$$q_{1111} = q_{2222} = 3q_{1122} = \frac{3}{8}(1 - 2q_{33} - q_{3333}).$$

Taking all these relations into account and discarding constant terms, we obtain

$$\frac{1}{4!}m_i m_j m_k m_\ell \Theta_{ijkl} = \alpha_1 m_z^2 + \alpha_2 m_z^4, \tag{34}$$

where

$$\begin{aligned}\alpha_1 &= \frac{N\eta_4}{280}[3 - 6q_{33} - 5q_{3333}] - \frac{N\eta_2^2}{200}[(3+q_{33})(1-3q_{33})],\\ \alpha_2 &= \frac{N\eta_4}{280}\left[\frac{3 - 30q_{33} + 35q_{3333}}{8}\right] - \frac{N\eta_2^2}{200}\left[\frac{1-3q_{33}}{2}\right]^2.\end{aligned} \tag{35}$$

Combining Eqs. (32)–(34) in the series expansion (15), we finally obtain the effective free energy, Eq. (14) for an axially symmetric problem

$$-\beta\mathcal{U}_{\text{eff}}(z,q) = \lambda_1 z + \lambda_2 z^2 + \lambda_3 z^3 + \lambda_4 z^4,$$

where from now on, we shall use $z \equiv m_z$ for simplicity of notation. The coefficients λ are functions of q

$$\lambda_1 = 2\sigma h + \frac{N\eta_3}{70}(5q_3 + q_{333}), \tag{36}$$

$$\lambda_2 = \sigma + \frac{N\eta_2}{20}(3q_{33} - 1) + \alpha_1, \tag{37}$$

$$\lambda_3 = \frac{N\eta_3}{70}\left(q_3 - \frac{5}{3}q_{333}\right), \tag{38}$$

$$\lambda_4 = \alpha_2. \tag{39}$$

Note that the terms involving z are not corrections of first order, but rather of third order; i.e., they depend on η_3. As will be shown, keeping terms up to third order is important to describe the phase transition to an ordered state. On the other hand, for simplicity we will usually neglect the fourth-order correction, which will not alter any of the basic conclusions.

For the purpose of modelling, it is also convenient to make the following changes. Define $p_\ell = \langle P_\ell(z)\rangle$ as the average of the Legendre polynomial of order ℓ on z. Also, define the new constants

$$\frac{N\eta_2}{10} = \gamma\sigma^2, \qquad \frac{2N\eta_3}{25} = \omega\sigma^3, \tag{40}$$

so that $\sigma = Kv/k_BT$ can be interpreted as a measure of inverse temperature. Then Eqs. (36)–(38) become

$$\lambda_1(p_1,p_3) = 2\sigma h + \omega\sigma^3 p_1 + \omega\sigma^3\frac{1}{14}p_3, \tag{41}$$

$$\lambda_2(p_2) = \sigma + \gamma\sigma^2 p_2, \tag{42}$$

$$\lambda_3(p_3) = -\frac{5}{42}\omega\sigma^3 p_3. \tag{43}$$

The effective free energy, we shall work with thus reads

$$-\beta\mathcal{U}_{\text{eff}}(z,P) = \lambda_1(p_1,p_3)z + \lambda_2(p_2)z^2 + \lambda_3(p_3)z^3. \tag{44}$$

For completeness, we also note that Eq. (35) becomes

$$\begin{aligned}\alpha_1 &= -\frac{N\eta_4}{280}\frac{8}{7}(6p_2 + p_4) + \frac{N\eta_2^2}{200}p_2(p_2+5),\\ \alpha_2 &= \frac{N\eta_4}{280}p_4 - \frac{N\eta_2^2}{200}p_2^2.\end{aligned}$$

The consistency relations for the equilibrium moments are now written in terms of $p_\ell = \langle P_\ell(z)\rangle$

$$p_\ell = \frac{\displaystyle\int_{-1}^{1} P_\ell(z)e^{\lambda_1(p_1,p_3)z + \lambda_2(p_2)z^2 + \lambda_3(p_3)z^3}\,\mathrm{d}z}{\displaystyle\int_{-1}^{1} e^{\lambda_1(p_1,p_3)z + \lambda_2(p_2)z^2 + \lambda_3(p_3)z^3}\,\mathrm{d}z}. \tag{45}$$

This is a set of 3 non-linear equations (for p_1, p_2, and p_3). They may be solved using Newton's method and the integrals on the right-hand side may be computed very efficiently using Gauss-Legendre quadrature. Once the first three coefficients have been computed, this same formula can be used to find all other p_ℓ.

V. QUALITATIVE DISCUSSION OF THE RELAXATION TIME

Before we go into the dynamical problem, where the relaxation time will be studied in more detail, let us stop to discuss some equilibrium properties of the system. For simplicity, we will assume an axially symmetric potential, so that the effective free energy is given by Eq. (44) with coefficients (41)–(43).

The original formula of Néel for the relaxation time is $\tau \sim e^\sigma$, where $\sigma = Kv/k_BT$; i.e., it depends on the term proportional to the uniaxial anisotropy. If we assume that the dipolar interaction is small, then we may retain only the first correction, which is actually contained in $\lambda_2 z^2$ and not $\lambda_1 z$. Suppose, also, that $h = 0$. The effective free energy in Eq. (44), thus, becomes that of a simple uniaxial anisotropy with effective anisotropy parameter $\lambda_2 = \sigma + \gamma\sigma^2 p_2 \sim \sigma + \gamma\sigma^2$, since $p_2 \sim 1$. The relaxation time in this case scales as

$$\tau \sim \exp(\sigma + \gamma\sigma^2). \tag{46}$$

Whence, we conclude that the first manifestation of the dipolar interaction is to increase the effective anisotropy barrier of the system and thence the relaxation time. It is also seen to depend quadratically on the inverse temperature.

A common correction to the Néel relaxation time, to include the dipolar interaction, is the Vogel-Fulcher law

$$\tau \sim \exp\left[\frac{Kv}{k_B(T - T_0)}\right], \tag{47}$$

where T_0 is a parameter that arises from the dipolar interaction. Expanding the term in the exponent in powers of T_0, we find

$$\frac{Kv}{k_B(T-T_0)} \simeq \frac{Kv}{k_BT} + \frac{Kv}{k_BT^2}T_0.$$

To estimate T_0, Shtrikman and Wohlfarth[39] argued as follows. For a small magnetic field H, the relaxation time is roughly approximated by

$$\tau \sim \exp\left[\frac{Kv}{k_BT} + \frac{\mu H}{k_BT}\right].$$

Due to the dipolar interaction, they proposed to replace H by its average

$$H \to \bar{H} = H \tanh\left(\frac{\mu H}{k_BT}\right) \simeq \frac{\mu H^2}{k_BT},$$

which results in

$$\tau \sim \exp\left[\frac{Kv}{k_BT} + \left(\frac{\mu H}{k_BT}\right)^2\right]. \tag{48}$$

This is precisely the first term in the cumulant expansion of Sec. III (assuming an axially symmetric potential *a priori*). It also has the same quadratic dependence on the temperature. Whence, the present model is seen to be in agreement with the Vogel-Fulcher law, which has been extensively tested experimentally. In a sense, it may be regarded as a generalisation of this law. Comparing Eqs. (47) and (48), we obtain the correction $T_0 = (\mu H)^2/(k_BKv)$. Since this field H is not usually known, this result cannot be compared to experimental data. On the other hand, using the present model, it becomes possible to express T_0 in terms only of known quantities

$$T_0 = \frac{N\mu^2}{10k_BKv}\left(\frac{\mu_0}{4\pi}\right)^2 \langle\mu^2\rangle\left\langle\frac{1}{R^6}\right\rangle. \tag{49}$$

In Ref. 42, Dejardin obtained a correction for the relaxation time of the form

$$\tau \sim \frac{e^\sigma}{1-\delta}, \tag{50}$$

where δ (in his paper called λ) is of the same order as η_1 in Eq. (22). Incorporating the denominator into the exponential and expanding as a series in δ yields

$$\tau \sim \exp\left\{\sigma + \delta + \frac{1}{2}\delta^2 + \ldots\right\}. \tag{51}$$

Since δ is proportional to $\beta = 1/k_BT$, this can be interpreted as a series in β, similar to the result here obtained. An important difference, however, lies in the fact that in Déjardin's result the first order correction to the dipolar interaction is linear in β, and not quadratic as in the present case or in Shtrikman and Wohlfarth's model just discussed.[39] However, this discrepancy is merely due to the fact that Déjardin's calculations involved an expansion carried only up to first order. If, instead, higher orders had been computed, then the parameter σ appearing in Eq. (51) would certainly be replaced by an effective anisotropy, similarly to that obtained here.

VI. FERROMAGNETIC ORDER

For sufficiently dense systems, including the third order corrections represented by ω, the present model predicts a phase transition to a ferromagnetic state. This is illustrated in Fig. 1, which shows curves of $p_1 = \langle z\rangle$ as a function of the inverse temperature parameter σ, with fixed $\gamma = 0.02$. These curves were computed numerically using Eq. (45). Fig. 1(a) contains curves for $h = 0$ and different values of ω. The observed phase transition is seen to be very similar to most mean-field theories of magnetic materials. In Fig. 1(b) similar results are shown, but with fixed $\omega = 1 \times 10^{-3}$ and varying applied field h.

To estimate the critical temperature (in terms of σ), we make use of the fact that, at the phase transition odd powers p_1, p_3, etc., vanish, whereas even powers p_2, p_4, etc., vary continuously. Expanding Eq. (45) for p_1 in terms of the odd powers and assuming $h = 0$ yields

$$p_1 \simeq \lambda_1\zeta + \lambda_3\zeta^2,$$

where

$$\zeta = \frac{\int z^2 e^{\lambda_2 z^2}\, dz}{\int e^{\lambda_2 z^2}\, dz}$$

is the average $\langle z^2\rangle$ above the transition (where the odd terms are zero). We have also approximated $\langle z^4\rangle \simeq \langle z^2\rangle^2$. Moreover,

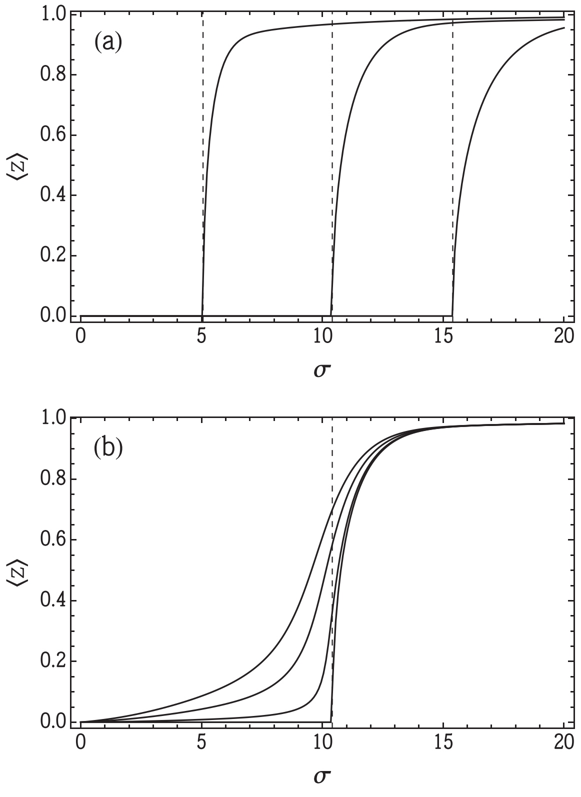

FIG. 1. Magnetisation $\langle z\rangle$ as a function of inverse temperature σ for $\gamma = 0.02$. (a) Applied field $h = 0$ and, from right to left, $\omega = 3 \times 10^{-4}$, 1×10^{-3}, and 1×10^{-2}. (b) Fixed $\omega = 1 \times 10^{-3}$ and, from bottom to top, $h = 0$, 1×10^{-3}, 5×10^{-3}, and 1×10^{-2}. Dashed lines illustrate the critical temperatures σ_{crit}.

since the even powers vary continuously at the transition, ζ is in fact close to q_{33}, the average over the full distribution. If we use $q_{333} \simeq q_{33} q_3 \simeq \zeta p_1$, we obtain the equation

$$\omega\sigma^3 \left\{ 1 - \frac{(3-5\zeta)^2}{84} \right\} \zeta = 1. \tag{52}$$

The second term is much smaller than the first and may be regarded as a correction. Neglecting it yields

$$\sigma \simeq 1/(\omega\zeta)^{1/3}. \tag{53}$$

In principle $\zeta = \zeta(\sigma)$. However, this dependence is weak and using $\zeta \sim 0.8$ suffices for a first approximation. This is illustrated in Fig. 2, where we show the critical temperature σ_{crit} as a function of ω for fixed $\gamma = 0.02$. These results were computed exactly by numerically solving Eq. (45). As can be seen, they show a good agreement with Eq. (53) when $\zeta = 0.8$.

VII. DYNAMICS

To introduce the mean-field approximation into the dynamics, we assume that the effective magnetic field h_e acting on the particle is the gradient of the effective free energy, Eq. (14). To illustrate the procedure, we will restrict the discussion to the axially symmetric system, where the effective energy is given by Eq. (44). In this case, we find

$$h_{\text{e}} = -\beta \frac{\partial \mathcal{U}_{\text{eff}}}{\partial z} = \lambda_1(p_1, p_3) + 2\lambda_2(p_2) z + 3\lambda_3(p_3) z^2, \tag{54}$$

where the coefficients λ are given by Eqs. (41)–(43). This field will then enter the Fokker-Planck equation for the distribution $f(z,t)$

$$2\tau_N \frac{\partial f}{\partial t} = \frac{\partial}{\partial z} \left\{ (1-z^2) \left[\frac{\partial f}{\partial z} - f(z,t) h_{\text{e}}(z) \right] \right\}, \tag{55}$$

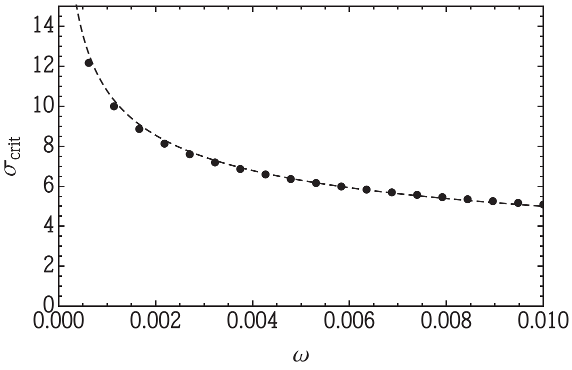

FIG. 2. Critical temperature σ_{crit} as a function of ω. Points correspond to the exact solution, manually obtained from Eq. (45) with $\gamma = 0.02$ and $h = 0$, whereas the dashed curve was computed from Eq. (53) with $\zeta = 0.8$.

where $\tau_N = \beta\mu(1+\alpha^2)/(2\gamma_0\alpha)$ is the Néel relaxation time, with α being the magnetic damping and γ_0 is the electron's gyromagnetic ratio. Now, let $g(z)$ be an arbitrary function of z. It can be shown[9] that its average satisfies

$$2\tau_N \frac{\mathrm{d}\langle g \rangle}{\mathrm{d}t} = \left\langle (1-z^2) h_e(z) \frac{\partial g}{\partial z} \right\rangle + \langle \Delta^2 g \rangle, \tag{56}$$

where Δ^2 is the angular part of the Laplacian in spherical coordinates. The common choice is $g(z) = P_\ell(z)$, so that $\langle g(z) \rangle = p_\ell$ and $\Delta^2 P_\ell(z) = -\ell(\ell+1) P_\ell(z)$. Using the relations $(1-z^2) P_\ell = \ell(P_{\ell-1} - z P_\ell)$ and

$$(2\ell+1) z P_\ell = (\ell+1) P_{\ell+1} + \ell P_{\ell-1}, \tag{57}$$

we may write Eq. (56) as

$$2\tau_N \frac{\mathrm{d}p_\ell}{\mathrm{d}t} = \frac{\ell(\ell+1)}{2\ell+1} \langle h_e(z)[P_{\ell-1}(z) - P_{\ell+1}(z)] \rangle - \ell(\ell+1) p_\ell. \tag{58}$$

Substituting Eq. (54) for $h_e(z)$ this may be further transformed to read

$$2\tau_N \frac{\mathrm{d}p_\ell}{\mathrm{d}t} = \frac{\ell(\ell+1)}{2\ell+1} (\mathcal{A}_1 + \mathcal{A}_2 + \mathcal{A}_3) - \ell(\ell+1) p_\ell. \tag{59}$$

The functions $\mathcal{A}$ are determined by repeated use of Eq. (57)

$$\begin{aligned}
\mathcal{A}_1 &= \lambda_1 (p_{\ell-1} - p_{\ell+1}), \\
\mathcal{A}_2 &= 2\lambda_2(p_2) \left[\frac{\ell-1}{2\ell-1} p_{\ell-2} + \frac{2\ell+1}{(2\ell-1)(2\ell+3)} p_\ell - \frac{\ell+2}{2\ell+3} p_{\ell+2} \right], \\
\mathcal{A}_3 &= 3\lambda_3(p_3) \left[\frac{(\ell-1)(\ell-2)}{(2\ell-1)(2\ell-3)} p_{\ell-3} + \frac{\ell^2+\ell-3}{(2\ell+3)(2\ell-3)} p_{l-1} \right. \\
&\quad \left. - \frac{\ell^2+\ell-3}{(2\ell-1)(2\ell+5)} p_{\ell+1} - \frac{(\ell+2)(\ell+3)}{(2\ell+3)(2\ell+5)} p_{\ell+3} \right].
\end{aligned} \tag{60}$$

The system of Eq. (59) constitutes an infinite hierarchy of differential recurrence relations. Upon truncation at some number n, it can be cast in the form of a system of ordinary differential equations for the (column) vector $\boldsymbol{p} = (p_1, p_2, \ldots, p_n)$. In the limit of infinite dilution both γ and ω are zero and the resulting system is linear

$$\frac{\mathrm{d}\boldsymbol{p}}{\mathrm{d}t} = A\boldsymbol{p} + \boldsymbol{b}, \tag{61}$$

where A is an $n \times n$ matrix and $\boldsymbol{b} = (2h/3, 4\sigma/5, 0, 0, \ldots)$ is a vector of length n. Otherwise, since the coefficients λ are functions of p, we have instead a non-linear system

$$\frac{\mathrm{d}\boldsymbol{p}}{\mathrm{d}t} = \boldsymbol{F}(\boldsymbol{p}), \tag{62}$$

where $\boldsymbol{F}(\boldsymbol{p})$ is a vector-valued function of $\boldsymbol{p}$. Alternatively, using the sum convention we could write this componentwise as

$$\frac{\mathrm{d}p_i}{\mathrm{d}t} = b_i + A_{ij} p_j + B_{ijk} p_j p_k.$$

The first two terms agree with the original terms in Eq. (61). The last term is a rank 3 tensor and contains quadratic combinations of the p_i.

In the infinitely diluted system, Eq. (61), the relaxation time is roughly proportional to the smallest non-vanishing eigenvalue of A. The solution of Eq. (61) is a sum of decaying exponentials and that corresponding to the smallest non-vanishing eigenvalue is dominant at the long-time limit. As for the non-linear problem in Eq. (62), the relaxation time is estimated by a linearisation near the fixed point, which is accomplished as follows. First compute the fixed point $\boldsymbol{p}^{(0)}$ which satisfies $\boldsymbol{F}(\boldsymbol{p}^{(0)}) = 0$. This can either be done directly, as the roots of a non-linear system of n equations, or using Eq. (45). The latter is more efficient, since it only requires the root of 3 equations (for p_1, p_2, and p_3). Next, expanding Eq. (62) around $\boldsymbol{p}^{(0)}$, we find

$$\frac{\mathrm{d}\boldsymbol{p}}{\mathrm{d}t} \simeq \frac{\partial \boldsymbol{F}}{\partial \boldsymbol{p}}\bigg|_{\boldsymbol{p}=\boldsymbol{p}^{(0)}} (\boldsymbol{p} - \boldsymbol{p}^{(0)}), \tag{63}$$

where $\partial\boldsymbol{F}/\partial\boldsymbol{p}$ is the Jacobian matrix, applied at the fixed point $\boldsymbol{p}^{(0)}$. The relaxation time is then roughly proportional to the reciprocal of the smallest eigenvalue ϵ_1 of this matrix

$$\tau \simeq 2\tau_N/\epsilon_1. \tag{64}$$

Fig. 3 shows the relaxation time as a function of σ for $\gamma = 0.02$ and different values of ω. When $\omega = 0$, one already observes a substantial enhancement of the relaxation time due to the first correction γ. This is seen by comparison with the dashed curve representing Brown's formula for the relaxation time of an infinitely diluted system

$$\tau = \tau_N \frac{\sqrt{\pi}}{2} \frac{e^{\sigma}}{\sigma^{3/2}}. \tag{65}$$

Irrespective of this increase, however, the system shows no phase transition as long as $\omega = 0$, i.e., τ remains finite for all σ. On the other hand, when $\omega \neq 0$, the relaxation time is seen to diverge at the critical temperature σ_{crit} (cf. Fig. 1). This divergence was also predicted by Déjardin in Ref. 42 which, in his model, is linked to the singularity present in Eq. (50) when $\delta \to 1$. The proposed values for γ and ω are merely illustrative, and it is reasonable to expect that in real systems this divergence would only take place at substantially higher values of σ. Nevertheless, the main point is that for a given ω, there exists a point σ_{crit}, approximately given by Eq. (53), for which the relaxation time diverges.

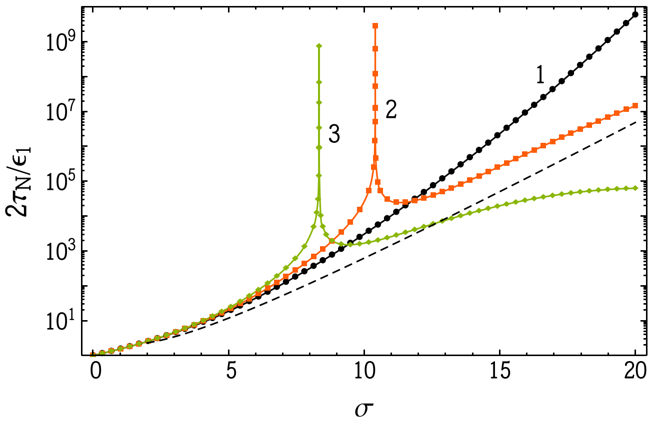

FIG. 3. Relaxation time, Eq. (64), as a function of σ, with $\gamma = 0.02$ and the following values of ω: (1) $\omega = 0$, (2) $\omega = 1 \times 10^{-3}$, and (3) $\omega = 2 \times 10^{-3}$. The dashed curve is Brown's original formula for the relaxation time, Eq. (65), which represents an infinitely diluted system with $\gamma = \omega = 0$.

VIII. DISCUSSION AND CONCLUSIONS

In the present paper, a mean-field approximation was presented to treat the effects of the dipolar interaction in systems of small magnetic particles. The main premise of the approximation was to introduce a new term in the free energy of a single reference particle, representing the average effect of the dipolar interaction due to the other particles in a sample. This reduces the many-body problem to that of a single-particle in a non-interacting ensemble. As a result, all of the machinery previously developed for non-interacting systems may be employed. In devising this new energy term, the random spatial orientation of the particles was used, commonly encountered in most real samples. It was argued that the dipolar field plays the role of a random field corresponding to a sum of independent identically distributed random variables. The result was an effective energy expressed as a cumulant expansion of this random field, which in the present case was carried up to fourth-order. While this could be extended to higher order cumulants with the same procedure, the calculations become increasingly cumbersome.

The model is able to correctly predict that the first manifestation of the dipolar interaction, in diluted systems, is in the form of an enhancement of the relaxation time. Further increasing the particle concentration leads to an ordered state, captured by the third order correction in the model. The properties of these two phenomena were studied in Secs. V and VI. Similar changes in the relaxation time were also predicted by several other authors, who developed similar mean-field approximations. In particular, the final result here obtained can be seen as a generalisation of the Vogel-Fulcher law, which may be viewed as a series expansion in powers of $\beta = 1/k_BT$ (see also Ref. 39). Moreover—to the author's knowledge at least—this is the first time where it is possible to identify the parameter T_0 appearing in the Vogel-Fulcher law with fundamental parameters of the samples, as in Eq. (49).

As for the phase transition, one may at first argue that it is in contradiction with one of the premises of the model; namely, that the magnetisation vectors of each particle are statistically uncorrelated. However, it is important to bear in mind that, as shown in Sec. III, this correlation would only manifest itself as a fourth-order correction whereas, for the description of the phase transition, it suffices to consider corrections only up to third order. Notwithstanding, marked differences are certainly expected between the properties predicted by the present model and those of real and strongly correlated systems, an ill to which most mean-field approximations suffer.

The procedure to introduce the mean-field approximation into the dynamics of the problem is standard: the effective field appearing in the Fokker-Planck equation, which is the gradient of the free energy, is simply replaced by the gradient of the new effective energy. There is, however, a fundamental difference for the effective energy depends itself on the statistical moments of the magnetisation. This yields a non-linear Fokker-Planck equation which, upon expansion in terms of statistical moments, results in a system of non-linear ordinary differential equations. In the present paper this was illustrated in the context of axially symmetric potentials, which was then applied to study the relaxation time in the presence of the dipolar interaction (Sec. VII).

In the general case of non-axially symmetric potentials, a difficulty arises in the expansion of the Fokker-Planck equation, which must now be carried out in terms of spherical harmonics. This is in principle feasible, but it is the author's impression that the result will be extremely cumbersome given the large number of terms involved.

For the axially symmetric potential, the numerical solution of the infinite hierarchy of differential recurrence relations is no more difficult than in the infinitely diluted case. It thus enables one to test the influence of the dipolar interaction in a variety of situations, such as magnetic hyperthermia, field cooling/zero-field cooling, etc. A more detailed investigation in this direction will be the subject of a future publication.

It is interesting to compare the present model with that of Déjardin[42] given that his formalism is entirely analogous to that presented here. The only difference lies in how one approaches the computation of the new term U_{dip} in the single-particle free energy. Whereas in the present model this was based on the expansion of the dipolar field, interpreted as a random variable, in his model it was instead the "magnetic charge" distribution of the material that was expanded. Thus, both models are expected to be entirely equivalent. The present approach was chosen much more for a matter of convenience, since the expansion using the random field is much easier to carry out for higher orders. On the other hand, the interpretation of the dipolar field as a random variable is embedded with a physical interpretation which is admittedly of limited extent. Conversely, Déjardin's approach carries a much deeper physical meaning, with the expansion being derived directly from Maxwell's equations.

The results presented were given in terms of moments such as $\langle \mu^k \rangle$ and $\langle 1/R^{3k} \rangle$ of the magnetic moment and the distance from the reference particle, respectively. For modelling purposes, the actual values of these quantities are not particularly relevant. On the other hand, when comparing with experiments, this may be of relevance. The magnetic moment is usually well described by the log-normal distribution [the diameter is log-normally distributed and powers of a log-normally distributed random variable are also log-normally distributed]. The same cannot be said of the distribution of the inter-particle distances, for which no closed formula has been agreed on.

To finish, let me discuss the connection between the present results and the experimental protocol used in Ref. 21 to quantify the strength of the dipolar interaction. There, the imaginary part $\chi''(\nu, T)$ of the AC susceptibility was measured as a function of temperature for several frequencies ν of the exciting field (with very small amplitude, ~1 Oe). They were then plotted as a function of $T\log(1/\nu\tau_0)$. For non-interacting systems the energy barrier is $E_b = Kv$. From the relation $\tau = \tau_0 \exp(Kv/k_B T)$ then follows that $E_b/k_B = T\log(\tau/\tau_0)$, where $\tau = 1/\nu$ is taken as the frequency of the experiment. The value of $\tau_0 \sim 10^{-9}$ s was adjusted, so that the curves of χ'' for different frequencies overlapped. From these results the energy barrier distribution was computed from[45]

$$f(E_b) \simeq \frac{6K}{\pi M_s^2} \frac{\chi''(\nu, T)}{E_b(\nu, T)}.$$

Since $E_b \propto v$, it is customary to expect that this distribution should be well adjusted by a log-normal distribution. As the authors have shown, however, while this were true for diluted samples, deviations were observed upon increasing the particle concentration. Let us discuss how these changes may be accounted for with the present model. It is simpler to define an effective energy barrier

$$\mathcal{E}_b = \sigma + \gamma\sigma^2.$$

Note that $\gamma\sigma^2 \propto v^2$ and not v^4, as formula Eq. (22) may at first imply: v is being interpreted as a random variable, which does not appear in $\langle \mu^2 \rangle$. We assume that σ is a random variable distributed, according to a log-normal distribution with parameters $\bar{\sigma}$ and δ_σ

$$f(\sigma) = \frac{1}{\sqrt{2\pi}\sigma\delta_\sigma} \exp\left\{-\frac{\log^2(\sigma/\bar{\sigma})}{2\delta_\sigma^2}\right\}.$$

If all that is required are the changes in the average energy barrier, $\langle \mathcal{E}_b \rangle$, then we easily find

$$\langle \mathcal{E}_b \rangle = \bar{\sigma} e^{\delta_\sigma^2/2} + \gamma\bar{\sigma}^2 e^{2\delta_\sigma^2}.$$

The full distribution of $\mathcal{E}_b$ is also easily computed and reads

$$f(\mathcal{E}_b) = \frac{1}{\sqrt{1 + 4\gamma\mathcal{E}_b}} \frac{1}{\sqrt{2\pi}\kappa(\mathcal{E}_b)\delta_\sigma} \exp\left\{-\frac{\log^2(\kappa(\mathcal{E}_b)/\bar{\sigma})}{2\delta_\sigma^2}\right\},$$

where

$$\kappa(\mathcal{E}_b) = -\frac{1}{2\gamma}\left(1 - \sqrt{1 + 4\gamma\mathcal{E}_b}\right).$$

In conclusion, a mean-field approximation was developed to treat the dipolar interaction in systems of magnetic nanoparticles randomly distributed in space. The agreement with other mean-field theories and experimental results was shown to be quite satisfactory. The generality with which it was developed should open the way for a variety of important investigations, regarding both equilibrium and dynamical properties of the system.

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